(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 October 2013 (31.10.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/163421 A1

(51) International Patent Classification:
G01N 17/00 (2006.01) *G01N 33/15* (2006.01)
G01N 33/02 (2006.01) *G01N 21/59* (2006.01)

(21) International Application Number:
PCT/US2013/038205

(22) International Filing Date:
25 April 2013 (25.04.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/639,309 27 April 2012 (27.04.2012) US

(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors: **JERNAKOFF, Peter**; 3527 Hopkins Drive, Wilmington, Delaware 19808 (US). **NIEDENZU, Philipp, Martin**; 5441 Doral Drive, Wilmington, Delaware 19808 (US). **STANCIK, Cheryl, Marie**; 6416 Apelehama Court, Diamondhead, Mississippi 39535 (US). **MILONE, Michael, Patrick**; 203 Lawrence Corner Road, Pittsgrove, New Jersey 08318 (US).

(74) Agent: **FEULNER, Gregory, J.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: METHODS FOR PRODUCING NEW PACKAGING DESIGNS BASED ON PHOTOPROTECTIVE MATERIALS

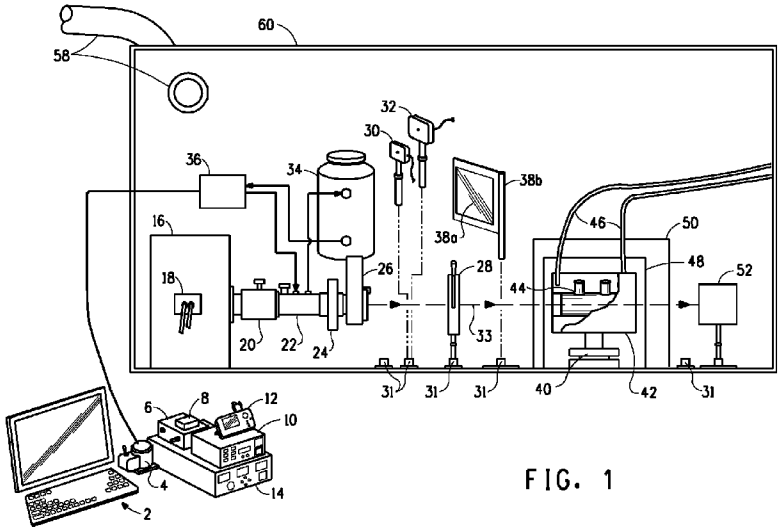

FIG. 1

(57) **Abstract**: This invention provides methods for quantification of photoprotective performance of packaging concepts in an accelerated timeframe. The methods can be used to generate models for the prediction of photoprotective performance values of untested materials based upon some other known qualitative or quantitative property. The methods use a light source which provides a light beam that impinges upon a photoprotective material (28) before being transmitted to a sample cell (44) comprising a photosensitive entity, such as a photosensitive nutrient.

WO 2013/163421 A1

TITLE

METHODS FOR PRODUCING NEW PACKAGING DESIGNS BASED ON PHOTOPROTECTIVE MATERIALS

This case claims priority back and is related to Application Number 61639309 having a filing date of April 27, 2012. Application Number 61639309 is hereby incorporated by reference.

FIELD OF THE INVENTION

This invention relates to the field of packaging technology, more specifically to methods and apparatus for testing materials for photoprotective properties.

BACKGROUND

It is well understood that certain compounds and nutrients contained within packages can be negatively impacted by exposure to light. Many different chemical and physical changes can result to molecular species as either a direct or indirect result of exposure to light, which can collectively be defined as photochemical processes. As described in Atkins, photochemical processes can include primary absorption, physical processes (e.g., fluorescence, collision-induced emission, stimulated emission, intersystem crossing, phosphorescence, internal conversion, singlet electronic energy transfer, energy pooling, triplet electronic energy transfer, triplet-triplet absorption), ionization (e.g., Penning ionization, dissociative ionization, collisional ionization, associative ionization), or chemical processes (e.g., disassociation or degradation, addition or insertion, abstraction or fragmentation, isomerization, dissociative excitation) (Atkins, P.W.; Table 26.1 Photochemical Processes. *Physical Chemistry*, 5th Edition; Freeman: New York, 1994; 908.). As one example, light can cause excitation of photosensitizer species (e.g., riboflavin in dairy food products) that can then subsequently react with other species present (e.g., oxygen, lipids) to

induce changes, including degradation of valuable products (e.g., nutrients in food products) and evolution of species that can adjust the quality of the product (e.g., off-odors in food products).

Protection of food, including its sensory quality and nutritional value, are of essential importance to society to protect our food supply and minimize food wastage thus ensuring sustainability in our food supply and distribution. Here sustainability considerations primarily include, but are not limited to, the cost, the use of non-renewable and renewable resources, environmental impacts, and water usage. The sustainability impact of food extends to include its production, packaging, distribution, usage, and waste accumulated through these processes. Furthermore, with the growing global population, sustainability also is related to food security and the nutritional value delivered by food.

As such, there is an art-recognized need to provide packaging with sufficient photoprotective properties to allow the protection of the package content(s). In certain studies, actual packaging systems and photochemical reactors have been used as a means to provide an indication of photoprotective performance of packaging concepts. However, generally these studies allow for the evaluation of only a single packaging concept and do not demonstrate sufficiently robust methods to allow for relative comparisons between experiments, nor the capability to produce performance design models based on the results.

For instance, the work of Kline *et al.* (Kline, M. A.; Duncan, S. E.; Bianchi, L. M.; Eigel, W. N., III; O'Keefe, S. F.; Light Wavelength Effects on a Lutein-Fortified Model Colloidal Beverage. *J. Agric. Food Chem.* 2011, *59*, 7203–7210) studying the light effects on a model colloidal beverage acknowledges the challenge to make relative comparisons between experimental conditions with their method due to changes in light intensity; however, they fail to demonstrate a suitable solution. Similarly, Webster *et al.* (Webster, J. B.; Duncan, S. E.; Marcy, J. E.; O'Keefe, S. F.; Effect of narrow wavelength bands of light on the production of volatile and aroma-active compounds in ultra high temperature treated milk. *Int.*

Dairy Journal. 2011, *21*, 305-311), studying the effects of light on milk, acknowledge the inability to make direct comparisons between all experiments due to differences in light energy output as a limitation of their capability (*see also* Webster, J. B.; Duncan, S. E.; Marcy, J. E.; O'Keefe, S. F.; Controlling Light Oxidation Flavor in Milk by Blocking Riboflavin Excitation Wavelengths by Interference. *J. Food Sci.* 2009, *74*, S390-S398). As another example, in a study by Palanuk (Palanuk, S. L.; Warthesen, J. J.; Smith, D. E.; Effect of agitation, sampling location and protective films on light-induced riboflavin loss in skim milk. *J. Food Sci.* 1988, *53*, 436-438), sampling location was shown to influence the results in studies of the effects of light on riboflavin in skim milk.

Additionally, studies in this field frequently require an extended testing period, such as days or weeks. For instance, Cladman (Cladman, W.; Scheffer, S.; Goodrich, N.; Griffiths, M. W.; Shelf-life of Milk Packaged in Plastic Containers With and Without Treatment to Reduce Light Transmission. *Int. Dairy Journal.* 1998, 8, 629-636) performed a study on photoprotective properties of materials that required a twenty day period to expose the samples. As another example, while Saffert *et al*. report two studies (Saffert, A.; Pieper, G.; Jetten, J.; Effect of Package Light Transmittance on the Vitamin Content of Pasteurized Whole Milk. *Packag. Technol. Sci.* 2006, *19*, 211–218; Saffert, A.; Pieper, G.; Jetten, J.; Effect of Package Light Transmittance on Vitamin Content of Milk. Part 2: UHT Whole Milk. *Packag. Technol. Sci.* 2008, *21*, 47–55.) that explore package performance related to retaining nutrients in milk, they conducted the study under conditions that required days of exposure.

There is an art recognized need to make determinations of the shelf life performance of food products contained within packages (Sensory Shelf Life Estimation of Food Products, G. Hough, CRC Press: Florida, 2010). It is desirable to make these determinations in an accelerated format. One current approach to accelerated shelf life determinations involves the use of higher storage temperature to accelerate the reactions within the food that lead to shelf life decline; however, these methods

requiring storage temperatures that are different from typical storage conditions are deficient in some cases as they do not allow the food system to be under storage temperatures that are relevant for retail storage. Furthermore, such higher storage temperatures may cause changes to the food (e.g., phase changes in the food system, changes to the conformations of molecules in this food) that limit the utility of such methods to provide accurate predictions in an accelerated time frame.

Given the above, a robust scientific method to rapidly quantify photoprotective performance of packaging concepts in a way that allows relative comparisons between the packaging concepts and is relevant to the conditions used for such packaging concepts in their targeted real-world applications is needed. These methods are needed to allow for the creation of performance design models for packaging concepts, and to allow for efficient design of photoprotective packages that achieve the required balance of performance attributes for a given package cost, weight, material usage, or other design requirements.

SUMMARY OF INVENTION

In one aspect, the present invention relates to a method for producing packaging designs comprising: (a) providing a known homogeneous liquid sample comprising one or more known photosensitive entities at appropriate concentrations; (b) providing a cell having controlled optical properties to contain the sample at a controlled temperature between about -20°C and about 100°C; (c) providing a light source that generates a light beam with a controlled spectral signature between about 290 and about 1000 nm and a controlled intensity between about 0.01 and about 5 W/cm^2; (d)placing the sample into the cell, rendering a sample cell; (e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative property; (f) exposing the shielded

sample cell to one or more light beam intensities for one or more durations; (g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points; (h) using the data points to determine a photoprotective performance value of the first test material; (i) repeating steps (a)-(h) with one or more additional test materials under the same conditions to generate one or more additional photoprotective performance values; (j) utilizing the two or more photoprotective performance values, more preferably more than two, to generate a model for a class of materials that relates that known qualitative or quantitative property to the photoprotective performance; (k) using the model of step (j) to identify a photoprotective performance value of a packaging material; and (l) using the packaging material in step (k) to design a package.

In another repect the present invention relates to a method of predicting the photoprotective performance of a material, the method comprising: (a) providing a sample comprising one or more photosensitive entities; (b) providing a cell having controlled optical properties to contain the sample at a pre-determined temperature between about -20°C and about 100°C; (c) providing a light source that generates a light beam with a spectral signature between about 290 and about 1000 nm and an intensity between about 0.01 and about 5 W/cm^2 as measured at a defined monitoring position; (d) placing the photosensitive entity into the cell, rendering a sample cell; (e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative property; (f) exposing the shielded sample cell to one or more light beam intensities for one or more durations; (g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points either by studying the sample while it is contained within said cell or by removing a sample for measurement by external

methods; (h) using the data points to determine a photoprotective performance value of the first test material; (i) repeating steps (a)-(h) with one or more additional test materials to generate one or more additional photoprotective performance values; (j) utilizing the two or more photoprotective performance values to generate a model for a class of materials with the known qualitative or quantitative property that predicts the photoprotective performance of an untested material within the same class based upon the known quantitative or qualitative property of the untested material; (k) using the model of step (j), for materials of the same class, predicting the unknown qualitative or quantitative property of a material based upon a known photoprotective performance value or predicting an unknown photoprotective performance value based upon a known qualitative or quantitative property of the material; (l) optionally using one or more values from step (h) or one or more models of step (j) to create a library of data which includes the photoprotective performance values as well one or more values describing the qualitative or quantitative properties of the material; (m) optionally using the library from step (l) to identify, describe, and/or predict properties of materials.

In still another respect, the present invention relates to a method for predicting the photoprotective performance of a material, the method comprising:(a) providing a known homogeneous liquid sample comprising one or more known photosensitive entities at appropriate concentrations; (b) providing a cell having controlled optical properties to contain the sample at a controlled temperature between about -20°C and about 100°C; (c) providing a light source that generates a light beam with a controlled spectral signature between about 290 and about 1000 nm and a controlled intensity between about 0.01 and about 5 W/cm^2;(d) placing the sample into the cell, rendering a sample cell; (e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative

property; (f) exposing the shielded sample cell to one or more light beam intensities for one or more durations; (g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points; (h) using the data points to determine a photoprotective performance value of the first test material; (i)repeating steps (a)-(h) with one or more additional test materials under the same conditions to generate one or more additional photoprotective performance values; (j)utilizing the two or more photoprotective performance values, more preferably more than two, to generate a model for a class of materials that relates that known qualitative or quantitative property to the photoprotective performance; and (k) using the model of step (j), to identify a photoprotective performance value of a packaging material.

In certain embodiments, the quantitative or qualitative property comprises one or more of the following: whiteness index ASTM E313; brightness index ASTM D985; CIE (1976) L*a*b* tri-stimulus data ASTM designation of E313 -10, D2244, E 1347, E1349, E1477, E2214, E284, E308, E805, E991, E1331, E275, D2616, D2745, D3134, D3964, D4877, D6290; DuPont Appearance Analyzer data; Diffuse Brightness of Paper and Paperboard (d/0) ASTM D2470; Standard test for haze for plastics ASTM D1003; Brightness, Directional (TAPPI) (T452); Brightness Directional; Brightness, Diffuse (T525); Brightness with Color (Diffuse(Micro TB1C) or Directional/ TAPPI(MicroS-5)); Printing & calculated TAPPI Opacity, Scattering & Absorption Coefficients, Sheet Brightness (T519); Directional / TAPPI Opacity, Scattering Coefficient, Absorption Coefficient (T425); T/dyne Micro TB-1C: Diffuse brightness, opacity, color, color difference, ASTM Index, & tristimulus; T/dyne Micro S-5 BOC:Dir/TAPPI brightness, opacity, color, color difference, ASTM Index, & tristimulus; Color, Hunter or CIE L*A*B* (State Directional or Diffuse Values), packaging material composition (e.g., polymer matrix for plastic packaging), packaging design paraemters (e.g., film thinckness for sheet

material), opacifying agent composition(s), and/or opacifying agent(s) loading as a design parameter.

In certain embodiments, preferred package designs providing efficient delivery of the desired properties (e.g., low cost materials, reduced weight materials) can be identified using the method.

In additional embodiments, the predictive models are used to facilitate the design of packages that provide photoprotection specific for the package contents. In other embodiments, the predictive models are used to assess sustainability metrics for a package design. For example, the methods could be used to allow for quantification, and thus optimization, of the impacts of parameters in package design (e.g., packaging material reduction or selection of alternative material choices) on sustainability impacts. In certain particular examples, the package contents include food, beverages, drugs, pharmaceuticals, and/or other nutrient-containing products.

In certain embodiments, the method further comprises correlating the changes to the one or more photosensitive entities in step (g) with one or more sensory evaluation criteria values and utilizing said predicted photoprotective performance to further predict one or more sensory evaluation criteria values of an untested material. Sensory evaluations comprise human evaluation of one or more of the following criteria: taste, texture, odor, or appearance.

In additional embodients, the library of data of step (l) and (m) can be used to aid in predicting packaging designs that provide desired qualitative or quantitative properties.

In further embodiments, the sample is maintained under one or both of controlled atmosphere conditions and under agitation, the exterior surface of the sample cell is maintained free from condensate, and/or the light beam is collimated.

In some embodiments, the one or more photosensitive entities are constituents of food, beverages, drugs, pharmaceuticals, or other nutrient-containing products. In other embodiments, the sample comprises one or

more photosensitive entities selected from natural and synthetic food additives, dyes, and pigments; chlorophyll; myoglobin, oxymyoglobin, and other hemeproteins; water and fat soluble essential nutrients, minerals, and vitamins; food components containing fatty acids; oils; proteins; pharmaceutical compounds; personal care and cosmetic formulation compounds and components; household chemicals and their components; and agricultural chemicals and their components. In additional embodiments, the sample comprises one or more photosensitive entities selected from 2, 3, 4, 5, 6, 7, 8, 9, 10, or more of the given classes.

In further embodiments, the measuring comprises a test method selected from the group consisting of HPLC (high performance liquid chromatography), GC (gas chromatography), IR (infrared) spectroscopy, NMR (nuclear magnetic resonance) spectroscopy, UV-VIS (ultra-violet, visible) spectroscopy, colorimetry, MS (mass spectrometry) coupled with other techniques (e.g., GC-MS and LC-MS), fluorescence spectroscopy, ion chromatography, thin layer chromatography (TLC), analytical wet chemistry, and/or electrochemical analysis (e.g., polarography, voltammetry). In particular embodiments, the measurement method is HPLC based which involves removal of a test aliquot from the sample cell. In another embodiment, the measurement method is UV-VIS spectroscopy based when sample analysis is performed while it is contained within the sample cell.

In another aspect, the present invention relates to a device for quantifying the photoprotective performance of a material, the device comprising: (a) a sample supply and control apparatus comprising: (I) a cell having controlled optical properties, the cell capable of containing a sample comprising one or more photosensitive entities; (II) a sample temperature sensor for monitoring the temperature of the sample within the cell; (III) a temperature control for maintaining the cell at a specified temperature set point that is chosen from the range between about -20°C and about 100°C with a deviation about the set point of less than 1°C; (IV) a dry air supply for delivering low-humidity air to one or more exposed

surfaces of the cell; and (V) an agitator for maintaining sample homogeneity within the cell; (b) a light generation and control apparatus comprising: (I) a light source, wherein the light source generates a light beam with a spectral signature between about 290 and about 1000 nm and an integrated intensity between about 0.01 and about 5 W/cm^2 as measured at a defined monitoring position; (II) a light beam collimating lens; (III) an infrared filter; (IV) a shutter; and (V) an iris; and (c) a test material holder positioned between the light generation and control apparatus and the sample supply and control apparatus such that, when a test material is placed in the test material holder, the light beam impinges upon the test material and any penetrating light impinges upon the cell.

In certain embodiments, the agitator comprises a magnetic stir bar within the cell and a magnetic stirring motor positioned below the cell. In other embodiments, the sample supply and control apparatus further comprises an atmosphere control and monitoring apparatus within the cell, wherein the atmosphere control and monitoring apparatus comprises a gas supply and metering device and an atmospheric sensor. In still further embodiments, the light generation and control apparatus further comprises a spectral filter.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 illustrates an embodiment of an apparatus useful in the present invention.

FIGS. 2A-2C illustrate more detailed views of particular elements of the illustrative embodiment of **FIG. 1**.

FIG. 3 illustrates an embodiment of a sample cell useful in the present invention.

FIG. 4 illustrates an embodiment of a dry-air supply apparatus useful in the present invention.

FIG. 5 illustrates a plot of the natural log of riboflavin concentration versus light exposure time for one exemplary test material experiment.

FIG. 6 illustrates a plot of mean pseudo-first order rate constant versus mean TAPPI opacity for one exemplary test material experiment.

DETAILED DESCRIPTION

It is to be understood that this invention is not limited to particular embodiments, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. Further, all publications referred to herein are incorporated by reference herein for the purpose cited to the same extent as if each was specifically and individually indicated to be incorporated by reference herein.

As used in this specification and the appended claims, terms in the singular and the singular forms "a," "an," and "the," for example, include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to "photosensitive entity," "the photosensitive entity," or "a photosensitive entity" also includes a plurality of photosensitive entities. Use of the term "a photosensitive entity" also includes, as a practical matter, many molecules of that photosensitive entity.

Additionally, as used herein, "comprising" is to be interpreted as specifying the presence of the stated features, integers, steps, or components as referred to, but does not preclude the presence or addition of one or more features, integers, steps, or components, or groups thereof. Thus, for example, a sample comprising a photosensitive entity may contain additional photosensitive entities or other components, such as other non-photosensitive nutrients. Additionally, the term "comprising" is intended to include examples encompassed by the terms "consisting essentially of" and "consisting of." Similarly, the term "consisting essentially of" is intended to include examples encompassed by the term "consisting of."

The present invention relates to devices and methods useful for determining and/or quantifying photoprotective properties of a material, and for making meaningful comparisons between such properties, by

quantifying the light-induced change or degradation of one or more photosensitive entities. In another embodiment, the method involves correlating a photoprotective performance value with another known quantitative or qualitative property of a material, such as the material's TAPPI Opacity or titanium dioxide content, to produce a predictive or correlative model. In another embodiment, the method further involves using the predictive or correlative model to assign a predicted photoprotective performance value to an untested material within the same material class based on the correlative property value.

The present apparatus allows for the accelerated testing of photoprotective properties. In certain embodiments, a test can be performed in a matter of hours while simulating the light exposure of several weeks under commercial food storage conditions. This method can thus be considered a high throughput screening method, as the testing rates can be accelerated over 100 times. In certain embodiments, the method and apparatus can be used to determine an optimum amount of light-protective agent, such as TiO_2, to include in a packaging material for photo-protection.

In certain other embodiments, this method can be useful to predict the results of sensory evaluations for a certain package concept, thereby avoiding the time and resources required to actually conduct sensory evaluation research on that package concept. Typically sensory evaluation research with human subject appraisers requires a large number of panelists and product assessments due to the limitations of the panelists' ability to accurately and precisely detect differences in sensory qualities of a product. As such, this type of evaluation of a packaging concept is generally both time consuming and costly. By using the methods of the present invention to predict the results of such a sensory evaluation, the present invention allows for predicted sensory evaluation results to be obtained in an accelerated timeframe and at a decreased cost.

The method and apparatus also provide a means to compare not-in-kind protective packaging solutions. For example, polymeric packaging films can be compared to paperboard.

FIGS. 1 and 2A-2C illustrate one possible embodiment of an apparatus of the present invention which is useful in the disclosed methods. The individual components of the overall apparatus are contained within an enclosure **60**, which is generally light blocking with regard to the spectra being analyzed during an experiment. To maintain proper atmospheric conditions (temperature, humidity, etc.) within the enclosure, the enclosure **60** possesses an exhaust fan and fan trunk **58**, which allows the air within enclosure **60** to be cycled at a desired interval and/or rate.

Within enclosure **60**, a light source, such as a lamp (not shown) contained within lamp housing **16**, is connected via appropriate electrical connections (not shown) to a light source power supply **14**, which in turn is connected via appropriate electrical connections (not shown) to a lamp controller **10**.

The light source can be any suitable light source to produce the desired light intensity, stability, and spectral characteristics. Depending upon the needs of the experiment, light sources employed may include incandescent light sources, fluorescent light sources, arc discharge lamps, LEDs (light emitting diodes), and/or laser light sources. For example, these light sources include but are not limited to carbon arc, mercury vapor, xenon arc, tungsten filament, or halogen bulbs. In one particular embodiment, the light source is a xenon arc lamp.

In certain embodiments, the light source is capable of providing an intensity of between about 0.001 W/cm^2 and about 5 W/cm^2 as measured at the defined monitoring position. In other embodiments, the light source is capable of providing an intensity of at least about 0.001 W/cm^2, 0.005 W/cm^2, 0.007 W/cm^2, 0.01 W/cm^2, 0.05 W/cm^2, 0.1 W/cm^2, 1 W/cm^2, 2.5 W/cm^2, or 5 W/cm^2 as measured at the defined monitoring position. In further embodiments, the light source is capable of providing an intensity

of not more than about 0.001 W/cm^2, 0.005 W/cm^2, 0.007 W/cm^2, 0.01 W/cm^2, 0.05 W/cm^2, 0.1 W/cm^2, 1 W/cm^2, 2.5 W/cm^2, or 5 W/cm^2 as measured at the defined monitoring position. In further embodiments, the light source is capable of providing an intensity between about 0.005 W/cm^2 and about 4 W/cm^2, between about 0.007 W/cm^2 and about 3 W/cm^2, between about 0.01 W/cm^2 and about 2.5 W/cm^2, between about 0.05 W/cm^2 and about 2 W/cm^2, or between about 0.1 W/cm^2 and about 1 W/cm^2 as measured at the defined monitoring position.

In other embodiments, the light source is capable of producing light with a spectral signature of about 200 nm to about 2000 nm. In other embodiments, the light source is capable of providing light at a wavelength of at least about 200 nm, 220 nm, 240 nm, 260 nm, 280 nm, 290 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800, nm, 900 nm, 1000 nm, 1250 nm, 1500 nm, 1750 nm, or 2000 nm. In further embodiments, the light source is capable of providing light at a wavelength of not more than about 200 nm, 220 nm, 240 nm, 260 nm, 280 nm, 290 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800, nm, 900 nm, 1000 nm, 1250 nm, 1500 nm, 1750 nm, or 2000 nm. In still further embodiments, the light source is capable of providing a spectral signature of about 220 nm to about 1750 nm, about 240 to about 1500 nm, about 260 to about 1250 nm, about 290 to about 1000 nm, about 200 to about 400 nm, about 350 to about 750 nm, or above about 750 nm.

In certain embodiments, the intensity and/or spectral characteristics of the light source are controlled and/or modified by one or more of a lens, a water-based infrared filter (to reduce the heat signature of the light beam), and a spectral filter. In one particular embodiment, the light from a lamp within lamp housing **16** travels through a collimating lens assembly **20**, then through an infrared filter **22**, which is a water-based infrared filter attached to water reservoir **34** and water pump **36**, the flow volume of which is controlled by a pump flow controller **4** to which water pump **36** is attached via appropriate electrical connections. The collimated and

infrared-filtered light then travels through an optical filter holder **24**, which can optionally contain an optical filter or filters to attenuate the light beam or portions thereof. Though the lens, infrared filter, and spectral filter(s) are shown in a particular order in **FIGS. 1 and 2a**, this is not to be taken as an indication that all of these components are required, nor that the indicated order is required. These components could be used in any desired order and/or in any desired combination, including employing none of them in the apparatus and method of the invention.

In certain embodiments, within enclosure **60**, a light source, such as a lamp (not shown) contained within lamp housing **16**, is connected via appropriate electrical connections (not shown) to a light source power supply **14**, which in turn is connected via appropriate electrical connections (not shown) to a lamp controller **10**. Lamp feedback monitor **18** is electrically connected to the lamp controller **10**. The lamp feedback monitor **18** communicates with the lamp controller **10** which in turn communicates with the light source power supply **14** to adjust the amount of power provided to the light source and/or in order to adjust the intensity of the light emanating from the light source.

In one embodiment, to ensure that the light beam possesses the proper intensity, a light power density sensor **30** can be positioned within the light beam, for instance removably positioned, using one of a plurality of holders **31** located along light path **33**. In a preferred embodiment, the light power sensor **30** can be removably positioned within the light beam using holder **72** and a suitably designed support apparatus. The light power density sensor **30** is attached via appropriate connections (not shown) to the optical energy meter **12**. Light power density sensor **30** can be inserted into an appropriate holder, so that a discrete intensity reading can be taken, for instance, prior to the initiation of an experiment and again after the termination of an experiment and/or at times during an experiment. This would allow the intensity of the light beam to be tested both before and after an experiment so that the user can ensure that the

power intensity was correctly set and did not significantly increase or decrease throughout the experiment.

In other embodiments, in order to ensure that the light beam possesses the proper spectral characteristics, a spectrometer sensor **32** can be removably positioned within the light beam using one of a plurality of holders **31** located along light path **33** or by using holder **72** and a suitably designed support apparatus. The spectrometer sensor **32** is attached via appropriate connections (not shown) to a spectrometer **8**. Spectrometer sensor **32** can be inserted into an appropriate holder , so that a discrete spectrometry reading can be taken, for instance, prior to the initiation of an experiment and again after the termination of an experiment. This would allow the spectral characteristics of the light beam to be tested before and after an experiment so that the user can ensure that the spectral characteristics were as desired and stable in the time frame of the experiment.

In another embodiment, part of the light beam can be directed away from light path **33** towards a suitable monitoring position (not shown) so as to allow monitoring of the light beam intensity and/or spectral characteristics during an experiment.

Light exposure initiation and cessation during operation of the apparatus or method can be controlled, for example, by a shutter mechanism **26**, the operation of which is controlled by a shutter controller **6**, to which it is attached via appropriate connections (not shown). Further, the cross sectional area of the light beam impinging upon a test material and/or sample can be adjusted by an iris **28** located within one of the plurality of holders **31**, which can be opened and closed as needed to produce a light beam of the desired diameter. Again, though these components are illustrated in **FIG. 1**, this should not be taken as an indication that one or all of them is required. For instance, the apparatus could be operated without a shutter by simply controlling initiation of the light beam through the lamp controller **10** and/or light source power supply

14. Similarly, the size of the light beam could be alternatively controlled, for example, through the collimating lens **20**.

Looking at **FIGS. 1, 2b, and 2c**, after passing through the iris **28**, the light beam will impinge upon a test material **38a**, which is held in place by material holder **38b**, which is in turn located within one of the plurality of holders **31** or more preferably holder **72**. The test material **38a** can be a material with certain known qualitative or quantitative properties, such as TAPPI Opacity or titanium dioxide content, or can be a completely unknown material. Further, the test material **38a** can be any material suitable for use as a packaging material or photoprotective material. Such materials include plastics (polymeric materials, e.g., low density polyethylene), glass, metal (e.g., cans, foils, or metalized layers), cellulosic materials (e.g., paper, paperboard), or combinations thereof in forms such as laminated structures, films (e.g., plastic wraps), sheets (e.g., papers), bags, sleeves, pouches, or rigid structures (e.g., bottles). These materials may also contain additives (e.g., pigments, printing inks, antioxidants) to provide additional appearance attributes or functionalities to the material. In certain embodiments, the material contains titanium dioxide. Materials tested could comprise an actual package, a portion of a packaging material, or a prototype of a portion of a packaging system including films, foils, plaques from rigid parts, papers, and laminated or composite structures of these materials.

The light transmitted by the test material **38a** will in turn impinge upon the sample cell **44**, which will be held in place during the experimental run by sample cell holder **42**, which optionally can be insulated so that it retains temperature more efficiently and effectively. Sample cell holder **42** is in direct contact with heat transfer block **48**, which is attached to thermoelectric device **50**, under the control of thermoelectric controller **51**. Thermoelectric device **50** can be either a heater or cooler, or a device that is capable of both heating and cooling. During operation, thermoelectric controller **51** directs a temperature set point for thermoelectric device **50**. Through heat transfer block **48**, the temperature

gradient (cold or heat) generated by thermoelectric device **50** is transferred to sample cell holder **42**. This allows the temperature within sample cell **44** to be maintained at a fixed temperature throughout an experimental run. Optionally, a heat transfer compound can be used to facilitate heat transfer between the sample cell **44** and the sample cell holder **42**. In certain embodiments, the temperature can be set at a temperature between about -20° C and about 100° C. In other embodiments, the temperature can be set at a temperature of at least about -20° C, -10° C, -5° C, -2° C, 0° C, 1° C, 2° C, 3° C, 4° C, 5° C, 6° C, 7° C, 8° C, 10° C, 25° C, 50° C, or 100° C. In further embodiments, the temperature can be set at a temperature of not more than about -20° C, -10° C, -5° C, -2° C, 0° C, 1° C, 2° C, 3° C, 4° C, 5° C, 6° C, 7° C, 8° C, 10° C, 25° C, 50° C, or 100° C. In still further embodiments, the temperature can be set at between about -10° C and about 50° C, about -5° C and about 25° C, about -2° C and about 10° C, about 0° C and about 8° C, about 1° C and about 7° C, about 2° C and about 6° C, about 3° C and about 5° C. In certain other embodiments, the temperature is set at about 4° C. In an embodiement, the deviation about the temperature set point is less than 1°C.

Sample cell **44** can comprise any suitable material and shape such that it possesses the desired optical characteristics. Preferably, sample cell **44** is optically transparent in the spectral range being investigated during the experiment. In certain embodiments, sample cell **44** is made of quartz. In certain embodiments, such as those shown in **FIGS. 1 and 3**, sample cell **44** can be substantially flat on one end, thereby allowing the light to impinge upon the sample cell at an angle that is substantially perpendicular to the flat end of the sample cell **44**, which can be a desirable optical situation. In certain embodiments, such as those shown in **FIGS. 1 and 3**, sample cell **44** can also be equipped with one or more access ports **43** to allow test samples, additives, or gases to be added or withdrawn from the cell and/or to allow sample cell thermocouple **56** or other probes or sensors to be inserted into sample cell **44** during an

experimental run. Sample cell thermocouple **56** is in turn attached, via appropriate connections, to temperature meter **62**. This can allow the temperature of the sample to be monitored and/or controlled throughout an experimental run. In certain embodiments, thermocouple **56** and/or temperature meter **62** is placed in communication with thermoelectric controller **51** such that the temperature can be automatically adjusted throughout an experimental run to maintain the sample at the desired temperature.

Further, access ports **43** could allow for an optional gas delivery tube and/or atmospheric sensor (not shown) to be inserted into the sample cell during an experimental run for monitoring and/or controlling the atmospheric conditions within sample cell **44** throughout the experimental run. Additionally, as illustrated in **FIGS. 1 and 2b**, directly below insulated sample cell holder **42** is a magnetic stirring motor **40**, which is attached via appropriate connections to a magnetic stirrer speed controller **54**. As shown in **FIG. 3**, this allows a magnetic stir bar **45** to be located within sample cell **44** during an experimental run so that the magnetic stirring motor can effectuate agitation of the sample at a desired speed throughout an experimental run, thereby ensuring substantial sample homogeneity.

As shown in **FIG. 1**, in certain embodiments, dry air, meaning air with relatively low humidity, can be supplied to the front and/or rear faces of sample cell **44** via delivery tubes **46** in order to prevent or reduce condensation forming on the sample cell. As used herein, the term “air” means atmospheric air or any other suitable gas, such as gaseous nitrogen. With reference to **FIG. 4**, air is supplied from supply **64**, via feed line **65**, to pressure regulator **66**. The air then continues through feed line **65** to flow valve **68** before traveling through drying chamber **70**. Drying chamber **70** can be any suitable type of apparatus for reducing humidity in air. For instance, in certain embodiments, drying chamber **70** can be a polycarbonate tube filled with a desiccant, such as “Drierite” desiccant. The reduced-humidity air then exits the drying chamber and travels via delivery tubes **46** to the faces of sample cell **44**, where it is released.

Any light that passes completely through sample cell **44** will eventually impinge upon beam stop **52**, which is constructed in such a way that it captures substantially all remaining light without allowing any significant portion of the light to reflect back toward the sample cell.

In certain embodiments, one or more of the components of the overall apparatus may be controlled or monitored by computer **2**. This can include one or more of light source power supply **14**, lamp controller **10**, pump flow controller **4**, water pump **36**, lamp output feedback detector **18**, optical energy meter **12**, shutter mechanism **26**, shutter controller **6**, iris **28**, spectrometer **8**, thermocouple **56**, temperature meter **62**, thermoelectric controller **51**, magnetic stirrer speed controller **54**, gas supply and metering device and atmospheric sensor (not shown), air supply **64**, or pressure regulator **66**.

During operation of the apparatus disclosed herein, a test material **38a** is placed within the material holder **38b** and one or more photosensitive entities is placed in the sample cell. Examples of test materials that can be investigated using the present invention include plastics (polymeric materials, e.g., low density polyethylene), glass, metal (e.g., cans, foils, or metalized layers), cellulosic materials (e.g., paper, paperboard), or combinations thereof in forms such as films (e.g., plastic wraps), sheets (e.g., papers), laminate structures, bags, sleeves, pouches, or rigid structures (e.g., bottles). These materials may also contain additives (e.g., pigments, printing inks, antioxidants) to provide additional appearance attributes or functionalities to the material. Packaging concepts would be comprised of these same materials and could comprise an actual package, a portion of a packaging material, or a prototype of a portion of a packaging system including films, foils, plaques from rigid parts, papers, and laminated or composite structures of these materials.

In certain embodiments, the photosensitive entity is a photosensitive nutrient. In particular embodiments, the photosensitive entity is selected from:

i. natural and synthetic food additives, dyes, and pigments (e.g., curcumin, erythrosine);
ii. chlorophyll (all variants);
iii. myoglobin, oxymyoglobin, and other hemeproteins;
iv. water and fat soluble essential nutrients, minerals, and vitamins (e.g., riboflavin, vitamin A, vitamin D);
v. food components containing fatty acids, particularly polyunsaturated fatty acids;
vi. oils (e.g., soybean oil);
vii. proteins (e.g., proteins derived from the amino acids tryptophan, histidine, tyrosine, methionine, cysteine, etc.);
viii. pharmaceutical compounds;
ix. personal care and cosmetic formulation compounds and their components;
x. household chemicals and their components; and
xi. agricultural chemicals and their components.

The species of interest could be studied in neat form or as a component of a solution or formulation. In certain embodiments, multiple photosensitive entities could be present, each at different concentrations. Different modes of light-induced change or degradation could occur in the system based upon the chemical nature of the photosensitive entities present to participate in the changes. For complete food systems, a combination of fats, oxygen, and photosensitive nutrients could be present to allow the interplay between multiple photosensitive entities and associated species to be observed upon light exposure. To allow for targeted and focused study as well as ease of analysis, model systems could be employed where only a single or a few components are included such that effects are isolated to a lesser number of components. Within a model system, a combination of entities that interact with light via different mechanisms could allow for a multidimensional assessment of light protection performance via a single experiment without the complexities of the study of a complete food system. Entities that interact with light via

pathways that involve singlet oxygen represent one class of photosensitive entities. Such a list is disclosed by Min *et al.* (Min, D. B. and Boff, J. M.; Chemistry and Reaction of Singlet Oxygen in Foods. *CRFSFS*. 2002, *1*, 58-72.). Other entities that themselves are photosensitizers (e.g., riboflavin), may allow for a different learning regarding light protection performance. In another embodiment, combinations of entities could be used to affect the rate of the changes occurring to the entities, for example the inclusion of a photosensitizer may accelerate the effect while the inclusion of an antioxidant may retard the effect. Thus, in certain embodiments, a single photosensitive entity could be present in the sample cell, while, in other embodiments, at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or more photosensitive entities can be simultaneously present and/or studied. In particular embodiments, the photosensitive entities present and/or studied include one or more photosensitive entities from 2, 3, 4, 5, 6, 7, 8, 9, 10 or all 11 of each of the following classes:

i. natural and synthetic food additives, dyes, and pigments (e.g., curcumin, erythrosine);
ii. chlorophyll (all variants);
iii. myoglobin, oxymyoglobin, and other hemoproteins;
iv. water and fat soluble essential nutrients, minerals, and vitamins (e.g., riboflavin, vitamin A, vitamin D);
v. food components containing fatty acids, particularly polyunsaturated fatty acids;
vi. oils (e.g., soybean oil);
vii. proteins (e.g., proteins derived from the amino acids tryptophan, histidine, tyrosine, methionine, cysteine, etc.);
viii. pharmaceutical compounds;
ix. personal care and cosmetic formulation compounds and their components;
x. household chemicals and their components; and
xi. agricultural chemicals and their components.

In particular embodiments, the photosensitive entities studied include one or more photosensitive entities from class i and ii, class i and iii, class i and iv, class i and v, class i and vi, class i and vii, class i and viii, class i and ix, class i and x, class i and xi, class ii and iii, class ii and iv, class ii and v, class ii and vi, class ii and vii, class ii and viii, class ii and ix, class ii and x, class ii and xi, class iii and iv, class iii and v, class iii and vi, class iii and vii, class iii and viii, class iii and ix, class iii and x, class iii and xi, class iv and v, class iv and vi, class iv and vii, class iv and viii, class iv and ix, class iv and x, class iv and xi, class v and vi, class v and vii, class v and viii, class v and ix, class v and x, class v and xi, class vi and vii, class vi and viii, class vi and ix, class vi and x, class vi and xi, class vii and viii, class vii and ix, class vii and x, class vii and xi, class viii and ix, class viii and x, class viii and xi, class ix and x, class ix and xi, class x and xi, or any combination thereof.

Each photosensitive entity can be present at a concentration of, for example, 0.0000001 wt% to 100 wt%. In certain embodiments, the photosensitive entity is present at a concentration of at least about 0.0000001 wt%, 0.000001 wt%, 0.00001 wt%, 0.0001 wt%, 0.001 wt%, 0.01 wt%, 0.01 wt%, 0.1 wt%, 1.0 wt%, 2.0 wt%, 3.0 wt%, 4.0 wt%, 5.0 wt%, 10.0 wt%, 20.0 wt%, 30.0 wt%, 40.0 wt%, 50.0 wt%, 60.0 wt%, 70.0 wt%, 80.0 wt%, 90.0 wt%, 95.0 wt%, 99.0 wt%, or 100.0 wt%. In certain embodiments, the photosensitive entity is present at a concentration of less than about 100.0 wt%, 99.0 wt%, 95.0 wt%, 90.0 wt%, 80.0 wt%, 70.0 wt%, 60.0 wt%, 50.0 wt%, 40.0 wt%, 30.0 wt%, 20.0 wt%, 10.0 wt%, 5.0 wt%, 4.0 wt%, 3.0 wt%, 2.0 wt%, 1.0 wt%, 0.1 wt%, 0.01 wt%, 0.001 wt%, 0.0001 wt%, 0.00001 wt%, 0.000001 wt%, or 0.0000001 wt%. The concentrations are dependent upon the species under evaluation and its typical concentration during practical applications and uses.

The sample cell and sample contained therein are brought to an appropriate temperature for the test, for example a temperature between about -20° C and about 100° C. Light produced by the light source, which has been optionally collimated, filtered, focused, and/or sized, at a desired

intensity (e.g., 0.01-5 W/cm^2 as measured at the defined monitoring position) and wavelength (e.g., 290-1000 nm) is then made to impinge upon the test material. The light that passes through the test material in turn impinges upon sample cell **44** and the sample contained therein.

Because the one or more entities within sample cell **44** are photosensitive, the light impinging upon them will cause some level of change which can be quantified at desired intervals either by measuring the sample while it is contained within sample cell **44** or by removing a test aliquot for measurement by external methods.. Suitable analytical methods for determining the amount of light-induced change or degradation include HPLC (high performance liquid chromatography), GC (gas chromatography), IR (infrared) spectroscopy, NMR (nuclear magnetic resonance) spectroscopy, UV-VIS (ultra-violet, visible) spectroscopy, colorimetry, MS (mass spectrometry) coupled with other techniques (e.g., GC-MS and LC-MS), fluorescence spectroscopy, ion chromatography, thin layer chromatography (TLC), analytical wet chemistry, and/or electrochemical analysis (e.g., polarography, voltammetry). In particular embodiments, the measurement method is HPLC based which involves removal of a test aliquot from sample cell **44**. In another embodiment, the measurement method is UV-VIS spectroscopy based when sample analysis is performed while it is contained within sample cell **44**. The experiment is continued for the desired length of time, with measurements performed at the desired intervals. The run time is a function of the nature of the photosensitive entity, environmental conditions (e.g., temperature and gas modification), and the analytical study of its associated rate of change. In certain embodiments, the experimental run time is less than 12 hours, less than 11 hours, less than 10 hours, less than 9 hours, less than 8 hours, less than 7 hours, less than 6 hours, less than 5 hours, less than 4 hours, less than 3 hours, less than 2 hours, less than 1 hour, less than 45 minutes, or less than 30 minutes.

The sampling intervals should be selected to obtain a minimum of two data points. In particular embodiments, the sampling intervals are

selected to obtain at least 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, or 50 data points. In certain embodiments the data points are distributed based on the anticipated sample reaction kinetics. Selected intervals will thus be dependent upon the rate of change of the photosensitive entities. In certain embodiments, the samples are extracted automatically via syringe pump or other suitable device and are delivered directly to vials or analytical equipment for analysis.

Once two or more measurements have been performed for an experimental run, the resulting data points tracking the change of the photosensitive molecule(s) or derivative product(s) can be used to assign a photoprotective performance value to the test material. Such photoprotective values can include, for instance, a pseudo-first order rate constant for light-induced change or degradation of the photosensitive entity being examined which can be converted to a light protection factor (LPF) via a suitable mathematical transformation. For example, LPF could be defined as the half-life of a photosensitive entity which is calculated, for example, for pseudo first order reaction kinetics by dividing ln(2) by the obtained pseudo-first order rate constant. Moreover, by regulating the variables of the experimental runs, such as light spectra, light intensity, light focus, duration of light exposure, sample temperature, sample homogeneity, and sample atmospheric conditions, results can be obtained with sufficient accuracy and precision to allow for quality run-to-run comparisons to be made.

In certain other embodiments, numerous test materials with one or more known quantitative or qualitative properties can be evaluated and a photoprotective performance value assigned to each such test material. The known quantitative or qualitative property can be, for example, a known concentration of opacifying agent (e.g., TiO_2) or a known reflectivity or opacity value (e.g., a TAPPI opacity value). In certain examples, the known quantitative or qualitative property or properties utilized in the predictive model include one or more of the following: whiteness

index ASTM E313; brightness index ASTM D985; CIE L*a*b* tri-stimulus data ASTM designation of E313 -10, D2244, E 1347, E1349, E1477, E2214, E284, E308, E805, E991, E1331, E275, D2616, D2745, D3134, D3964, D4877, D6290; DuPont Appearance Analyzer data; Diffuse Brightness of Paper and Paperboard (d/0) ASTM D2470; Standard test for haze for plastics ASTM D1003; Brightness, Directional (TAPPI) (T452); Brightness Directional; Brightness, Diffuse (T525); Brightness with Color (Diffuse(Micro TB1C) or Directional/ TAPPI(MicroS-5)); Printing & calculated TAPPI Opacity, Scattering & Absorption Coefficients, Sheet Brightness (T519); Directional / TAPPI Opacity, Scattering Coefficient, Absorption Coefficient (T425); T/dyne Micro TB-1C: Diffuse brightness, opacity, color, color difference, ASTM Index, & tristimulus; T/dyne Micro S-5 BOC:Dir/TAPPI brightness, opacity, color, color difference, ASTM Index, & tristimulus; Color, Hunter or CIE L*A*B* (State Directional or Diffuse Values), opacifying agent composition(s), and/or opacifying agent(s) loading. Where a correlative behavior is observed and modeled for a class of materials, the model can be used for a material within said class to predict the unknown qualitative or quantitative property of said materials based upon a known photoprotective performance value or to predict their an unknown photoprotective performance value based upon a known qualitative or quantitative property of the material. For instance, several test materials with known TAPPI opacity values and/or known TiO_2 concentrations could be evaluated using the apparatus and methods disclosed herein, and a photoprotective performance value assigned to each. The photoprotective performance values and TAPPI opacity or TiO_2 concentration values of these materials can in turn be used to generate a metric or predictive model that predicts the photoprotective performance value of a material based upon its TAPPI opacity and or TiO_2 concentration. This metric or model can then be used to predict the photoprotective performance vale of an untested material of the same class with a known TAPPI Opacity or TiO_2 content.

EXAMPLES

Example 1.

The ANOVA Gage Repeatability and Reproducibility (R&R) measurement systems analysis methodology employs an analysis of variance (ANOVA) random effects model to understand the measurement system capability. In a Gage R&R study, the amount of variability observed in measurements by the measurement system is compared to the total variability observed. Gage R&R study methodologies were applied to assess the repeatability and reproducibility of the device of **FIG. 1** used with the method disclosed herein. This study was designed and analyzed using Minitab software.

The Gage R&R study involved replicate evaluation of each of five film samples, or parts, by two different operators. These twenty separate experiments were conducted in random order within operators.

In this Gage R&R study, the following method conditions were fixed:

- Photosensitive Entity: Riboflavin dissolved in pH 6.4 aqueous phosphate buffer solution at a target concentration of 30.5 ± 1.5 mg/L
- Temperature: 4 ± 1°C
- Atmosphere: Air
- Light Power Density: 0.375 ± 0.005 W/cm^2 as measured at the holder **31** monitoring position that is located along light path **33** and is 6 inches from shutter **26** and 4 inches from iris **28**
- Sampling Times: samples withdrawn after 0, 10, 40, 80, 120, 160, and 200 minutes of light exposure
- Photosensitive Entity Analysis Method: HPLC analysis of removed sample aliquots for their riboflavin concentration

The test materials used for the study consisted of titanium dioxide pigmented low density polyethylene (LDPE) films prepared by cast film extrusion of approximately 48 μm thickness. Film swatches of about 6 cm by 13 cm were cut from a larger film sample for study. Each swatch was evaluated with light exposure only once. After evaluation, each swatch was

set aside for additional measurements including replicate measures of TAPPI opacity and film thickness where average values are reported.

The output of each run was the pseudo-first order rate constant of riboflavin decomposition. The decomposition of riboflavin in dilute aqueous solution under ambient atmosphere (i.e., excess of O_2 available for reaction as a dissolved gas in the solution) has been shown to follow pseudo-first order rate kinetics when said solution is exposed to UV or visible light (e.g., Ahmad, I.; Fasihullah, Q.; Noor, A; Ansari, I. A.; Ali, Q. Nawab Manzar, International Journal of Pharmaceutics (2004), 280(1-2), 199-208). More specifically, under conditions during which the energy distribution of light that is incident upon said solution is held constant, said decomposition can be described by the following integrated rate expression:

Eq. 1 $Ln[Riboflavin]_t = (-k' \times t) + Ln[Riboflavin]_0$

where:

$[Riboflavin]_t$ = Riboflavin concentration at time = t

$[Riboflavin]_0$ = Initial riboflavin concentration prior to light exposure

t = Light exposure time

k' = Pseudo-first order rate constant

When such reaction kinetics are observed, a plot of $Ln[Riboflavin]_t$ versus exposure time yields a straight line, the slope of which is the desired pseudo-first order rate constant. For this work, the rate constant plot was constructed using Minitab software, and the desired slope data was extracted using the Minitab 'Fitted Line Plot' analysis tool. The correlation coefficient (R^2) values indicating the quality of the linear fit derived from the linear regression analyses were all 98.5% or greater, showing excellent agreement of the data to the linear model. A sample of these data is shown in **FIG. 5** and the complete set of reduced data from each of the plots generated as such is presented in Table 1.

Table 1. Gage R&R Data

Run Order	Test Material	Operator	Rate Constant (min^{-1})	Average TAPPI Opacity (%)	Average Film Thickness (in)
1	O1	1	0.0180	28.04	0.00188
2	O4	1	0.0029	66.47	0.00185
3	O5	1	0.0018	78.82	0.00189
4	O2	1	0.0087	39.87	0.00186
5	O3	1	0.0047	52.88	0.00183
6	O1	2	0.0195	28.17	0.00184
7	O5	2	0.0016	78.71	0.00204
8	O4	2	0.0029	66.28	0.00190
9	O3	2	0.0045	52.17	0.00188
10	O2	2	0.0084	39.88	0.00190
11	O1	1	0.0199	28.22	0.00188
12	O5	1	0.0020	79.11	0.00196
13	O4	1	0.0035	65.55	0.00184
14	O2	1	0.0098	39.20	0.00183
15	O3	1	0.0047	53.10	0.00193
16	O1	2	0.0196	28.42	0.00189
17	O3	2	0.0050	52.77	0.00190
18	O5	2	0.0019	79.20	0.00193
19	O4	2	0.0031	66.02	0.00193
20	O2	2	0.0084	40.08	0.00191

The Gage R&R ANOVA analysis was conducted on the data presented in Table 1. The analysis outputs are shown in Table 2. This analysis revealed that 0.58% of the total contribution and 7.6% of the total study variability can be attributed to the measurement system with the remainder due to inherent (and by design) part-to-part variations. With a 95% confidence level for the data interpretation, neither operator-to-operator differences nor operator-part interactions were observed in this study (Operator ANOVA 'p' value = 0.661 with operator-part interactions

included; Operator * part ANOVA 'p' value = 0.445). Thus, this study demonstrated that the measurement system is capable of producing reproducible and repeatable data.

Table 2: Minitab Analysis Outputs of the ANOVA Analysis of the Gage R&R Study

Source	VarComp	%Contribution (of VarComp)
Total Gage R&R	0.0000003	0.58
Repeatability	0.0000003	0.58
Reproducibility	0.0000000	0.00
Operators	0.0000000	0.00
Part-To-Part	0.0000496	99.42
Total Variation	0.0000499	100.00

Source	Study Var StdDev (SD)	Study Var (6 * SD)	%Study Var (%SV)
Total Gage R&R	0.0005382	0.0032292	7.62
Repeatability	0.0005382	0.0032292	7.62
Reproducibility	0.0000000	0.0000000	0.00
Operators	0.0000000	0.0000000	0.00
Part-To-Part	0.0070455	0.0422727	99.71
Total Variation	0.0070660	0.0423959	100.00

Number of Distinct Categories = 18

The Gage R&R results thus suggest that the measurement system will yield riboflavin degradation rate constant data of adequate quality. This conclusion can be reasonably extended to other riboflavin based exposure studies that involve reasonable deviations away from the exposure conditions utilized in this Gage R&R study. Examples of such deviations include modifications to the following: the light power density and/or

spectral distribution that are incident upon the light attenuating test material, the riboflavin solution temperature, the initial riboflavin solution concentration and the test material composition. Additional extensions include other (i.e., non-riboflavin) photosensitive entities that may or may not exhibit pseudo-first order light-induced change or degradation rate kinetics and that may or may not be dissolved in water.

Example 2.

The rate constant data from Example 1 are analyzed along with additional characterization of the film swatches. The rate constant data in Table 1 are plotted in **FIG. 6** along with a fitted data model. This data model was fitted to the data points to yield a photoprotective model as a function of TAPPI Opacity.

This plot and model demonstrate that the light protection performance (*i.e.*, the ability to protect riboflavin from light-induced degradation) of the titanium dioxide loaded LDPE films utilized in this study can indeed be linked to the TAPPI Opacity values of said films, a relationship that is well described by a power law model. This demonstrates that for this type of material that TAPPI Opacity can be used to predict light protection performance. This method could be applied to other materials.

These type of data can in turn be used in the method of the present invention to confidently predict the light protection performance for test material comprised of the same or comparable titanium dioxide and LDPE materials in different relative amounts with a known TAPPI opacity.

Example 3.

The same method conditions were utilized as in Example 1, but the evaluated samples were two pieces (each evaluated in duplicate) derived from the same titanium dioxide pigmented, high density polyethylene (HDPE) bottle (1.8 wt% titanium dioxide, 1380 μm wall thickness, 97.9% TAPPI Opacity) and HPLC analysis was performed after 0, 10, 25, 50, 75,

100, and 125 minutes of light exposure. The R^2 values obtained from the linear regression analyses were all 98.5% or greater and a mean pseudo-first order rate constant of 0.000691 min^{-1} for riboflavin decomposition was found.

Example 4.

The same method conditions were utilized as in Example 3, but the evaluated samples consisted of four film swatches (each evaluated once) derived from the same piece of titanium dioxide pigmented, low density polyethylene film (1.0 wt% titanium dioxide, 47 μm thick, 39% TAPPI Opacity) and two of the swatches were evaluated at 14 ± 1 °C. The R^2 values obtained from the linear regression analyses were all 99.3% or greater and the 4 °C and 14 °C mean pseudo-first order rate constants were found to be 0.0112 min^{-1} and 0.0154 min^{-1}, respectively, indicating the sensitivity of temperature on the riboflavin degradation kinetics as consistent with the theoretical predictions given by the Arrhenius equation.

Example 5.

The same method conditions were utilized as in Example 3, but the evaluated samples consisted of four film swatches (each evaluated once) derived from the same piece of titanium dioxide pigmented, low density polyethylene film (1.0 wt% titanium dioxide, 47 μm thick, 40% TAPPI Opacity) and two of the swatches were evaluated using a UV light filter attenuated light beam (essentially complete wavelength cutoff at 385 nm and below), said beam possessing a light power density of 0.287 W/cm^2. The R^2 values obtained from the linear regression analyses were all 99.3% or greater and the mean pseudo-first order rate constants with and without the UV light attenuating filter in the light beam were found to be 0.0062 min^{-1} and 0.0112 min^{-1}, respectively, indicating the sensitivity of riboflavin degradation kinetics to the presence of UV light.

Example 6.

The same method conditions were utilized as in Example 3, but the evaluated samples consisted of four film swatches (each evaluated once) derived from the same piece of titanium dioxide pigmented, low density polyethylene film (1.0 wt% titanium dioxide, 47 μm thick, 40% TAPPI Opacity) and two of said swatches were evaluated using a reduced light power density of 0.201 W/cm^2. The R^2 values obtained from the linear regression analyses were all 99.3% or greater and the mean pseudo-first order rate constants for light power densities of 0.375 W/cm^2 and 0.201 W/cm^2 were found to be 0.0112 min^{-1} and 0.0045 min^{-1}, respectively, indicating the sensitivity of riboflavin degradation kinetics to light power density.

Example 7.

The same method conditions were utilized as in Example 3, but the evaluated samples consisted of four film swatches (each evaluated once) derived from the same piece of titanium dioxide pigmented, low density polyethylene film (2.0 wt% titanium dioxide, 50 μm thick, 53% TAPPI Opacity) and two of the swatches were evaluated under an atmosphere of carbon dioxide (< 0.2 ppm oxygen in the test solution after 15 minutes of CO2 sparging; oxygen levels in test solution were measured with an Ocean Optics – Dunedin, Florida - NeoFox oxygen sensor). The R2 values obtained from the linear regression analyses were all 98.4% or greater. The air atmosphere and carbon dioxide atmosphere mean pseudo-first order rate constants were found to be 0.0057 min-1 and 0.0172 min-1, respectively, indicating the sensitivity of the light induced degradation kinetics of riboflavin to the atmosphere present in the sample cell.

Example 8.

The same method conditions were utilized as in Example 3, but the evaluated samples consisted of two film swatches (each evaluated once) derived from the same piece of titanium dioxide pigmented, low density polyethylene film (2.0 wt% titanium dioxide, 47 μm thick, 53% TAPPI Opacity), the initial riboflavin concentration was 15 mg/L, the light intensity was 0.600 W/cm2 at the film swatch position and HPLC analysis of the sample cell solution was replaced by an in-situ UV-VIS spectroscopic analysis (riboflavin absorbance data at 447 nm captured every minute for 60 minutes) using a fiber dip probe (Model # FDP-200-0.22-1.5-S; B&W Tek, Inc., Newark, Delaware) inserted into said solution for the duration of the light exposure experiment. Rate constant data were calculated as

indicated in Example 1 substituting absorbance values for concentration values in Equation 1. The R2 values obtained from the linear regression analyses were all 99.7% or greater. A mean pseudo-first order rate constant of 0.0050 min-1 was found indicating that the generation of degradation rate data for a light exposed, photosensitive entity can be obtained without the need to remove material from the sample cell.

Example 9.

The light protection performance of an untested material of known TAPPI opacity within the same class of materials of that used to construct the photoprotective model of Example 2 (**FIG. 6**) is predicted using said model. The TAPPI opacity of the untested material was measured to be 35.95%. The model predicts a k' value 0.0112 min^{-1}. The k' value of the untested material was measured to be 0.0111 min^{-1} using the method of Example 1 with the HPLC analyses performed after 0, 10, 25, 50, 75, 100, and 125 minutes of light exposure. These results demonstrate that the photoprotective model is useful for the prediction of light protection performance based upon TAPPI opacity.

Example 10.

Each of three injection molded pigmentary titanium dioxide filled, high density polyethylene (HDPE) bottles (bottle dimensions: 7.16" high x 3.29" wide x 2.1" deep; total bottle internal volume: 528 mL), said bottles differentiated by TAPPI opacity value (achieved by adjusting their titanium dioxide loading), were each cut apart to yield one flat, rectangularly shaped plaque per bottle (plaque dimensions: ~10.9 cm long by ~6.4 cm wide by ~1232 microns thick). A fourth bottle of the same dimensions and composition as the first three but unpigmented was similarly cut apart and the resulting plaque then completely covered on one side by a thin (~15 microns) sheet of aluminum foil. The four plaques, coded X, Y, Z and F (the latter code denoting the foil wrapped, unpigmented plaque), were evaluated in duplicate for their light protection properties using the method conditions described in Example 1 with the exception that the samples for HPLC analyses were withdrawn at 0, 10, 25, 50, 75, 100 and 125 minutes

of light exposure and the light power density utilized was 0.425 ± 0.005 W/cm^2. The average pseudo-first order rate constant (k') value for riboflavin degradation that was obtained for each of the plaques is shown in Table 3.

Table 3. Average Pseudo-First Oder Rate Constant (k') Values

Plaque Code	TAPPI Opacity (%)	k' (day^{-1})
X	81.4	3.19
Y	92.4	1.70
Z	99.2	0.60
F	99.7	0.28

Example 11.

Multiple intact bottles of the same dimensions and compositions as the four studied as excised plaques in Example 10 were sanitized with an aqueous solution of bleach (100 ppm chlorine), thoroughly rinsed with deionized/distilled water and drained. Milk products, specifically 2% milk and 2% milk fortified with omega-3 fatty acids, were separately packaged into said bottles shortly after standard beverage processing with efforts being made to avoid light exposure. The filled bottles were then sealed with sanitized caps. A complete aluminum foil wrap was then applied to each of the filled, unpigmented HDPE bottles. Coding of the filled bottles mirrored that utilized in Example 10. This activity yielded eight separate sample bottle groups each one representing a different bottle code/milk product combination (four different bottle codes x 2 different milk products). Said groups were then simultaneously and randomly placed into a single walk-in, lighted, chilled dairy case (Friedrich Floating Air beverage case, Model # 60-10-1056, San Antonio, TX) for a 5 week long, simulated retail storage exposure study. During said study, the light intensity (sampled at three different interior locations) and temperature inside said case were found to be 1122 ± 439 lux and 2.7 ± 0.8 °C, respectively. Depending on sampling location, the light intensity in the interior of the case ranged from a low of 355 lux to a high of 1942 lux. At pre-determined times, two bottles were randomly selected from each of the eight sample bottle groups and removed from the dairy case. The contents of said bottles were then analyzed in triplicate in a spectrofluorometer (Shimadzo

Scientific Instrument, Inc., Columbia, MD) for riboflavin concentration while following a modification of the Association of Analytical Communities (AOAC) method 960.65 (See also Webster, JB, Duncan, SE, Marcy, JE, O'Keefe, SF. 2009. Controlling light oxidation flavor in milk by blocking riboflavin excitation wavelengths by interference. J. Food Sci. 74:390-398.; Bradley, RL. 2000. Dairy Products. In: William Horwitz W, editor. Official Methods of Analysis of AOAC Intl. Vol. II. 17th ed. Gaithersburg, Md.: AOAC Int. 1–83.). The obtained riboflavin concentration versus light exposure time data is reported in Table 4.

Table 4. Riboflavin Concentrations of Milk Products in Dairy Case Storage

Days of Storage	Milk Product	Bottle Code	Riboflavin Concentration (ug/mL)
0	2% Milk	F	23.92
0	2% Milk	F	24.51
1	2% Milk	F	23.72
1	2% Milk	F	23.62
3	2% Milk	F	24.00
3	2% Milk	F	25.20
8	2% Milk	F	24.60
8	2% Milk	F	23.60
15	2% Milk	F	21.24
15	2% Milk	F	22.17
22	2% Milk	F	22.83
22	2% Milk	F	22.61
29	2% Milk	F	23.30
29	2% Milk	F	22.91
36	2% Milk	F	22.50
36	2% Milk	F	21.80
0	2% Milk	X	23.92
0	2% Milk	X	24.51
1	2% Milk	X	23.46
1	2% Milk	X	23.57
3	2% Milk	X	21.30
3	2% Milk	X	21.00
8	2% Milk	X	16.80
8	2% Milk	X	18.30
15	2% Milk	X	15.23
15	2% Milk	X	13.85
22	2% Milk	X	12.96
22	2% Milk	X	13.16
29	2% Milk	X	14.28
29	2% Milk	X	14.37
36	2% Milk	X	5.85
36	2% Milk	X	7.58
0	2% Milk	Y	23.92
0	2% Milk	Y	24.51
1	2% Milk	Y	23.44
1	2% Milk	Y	23.40

3	2% Milk	Y	23.80
3	2% Milk	Y	22.50
8	2% Milk	Y	20.40
8	2% Milk	Y	19.10
15	2% Milk	Y	16.75
15	2% Milk	Y	20.75
22	2% Milk	Y	20.13
22	2% Milk	Y	16.07
29	2% Milk	Y	16.59
29	2% Milk	Y	16.37
36	2% Milk	Y	18.02
36	2% Milk	Y	18.16
0	2% Milk	Z	23.92
0	2% Milk	Z	24.51
1	2% Milk	Z	23.67
1	2% Milk	Z	22.80
3	2% Milk	Z	23.20
3	2% Milk	Z	24.20
8	2% Milk	Z	19.00
8	2% Milk	Z	21.30
15	2% Milk	Z	20.53
15	2% Milk	Z	21.37
22	2% Milk	Z	22.55
22	2% Milk	Z	22.15
29	2% Milk	Z	21.69
29	2% Milk	Z	21.27
36	2% Milk	Z	13.72
36	2% Milk	Z	18.70
0	2% Milk with Omega-3	F	23.75
0	2% Milk with Omega-3	F	23.67
1	2% Milk with Omega-3	F	23.09
1	2% Milk with Omega-3	F	23.27
3	2% Milk with Omega-3	F	22.85
3	2% Milk with Omega-3	F	22.71
8	2% Milk with Omega-3	F	20.78
8	2% Milk with Omega-3	F	19.90
15	2% Milk with Omega-3	F	21.18
15	2% Milk with Omega-3	F	21.48
22	2% Milk with Omega-3	F	21.04
22	2% Milk with Omega-3	F	20.90
29	2% Milk with Omega-3	F	18.28
29	2% Milk with Omega-3	F	17.94
36	2% Milk with Omega-3	F	17.61
36	2% Milk with Omega-3	F	14.88
0	2% Milk with Omega-3	X	23.75
0	2% Milk with Omega-3	X	23.67
1	2% Milk with Omega-3	X	20.97
1	2% Milk with Omega-3	X	20.98
3	2% Milk with Omega-3	X	14.53
3	2% Milk with Omega-3	X	14.03
8	2% Milk with Omega-3	X	11.43
8	2% Milk with Omega-3	X	10.99
15	2% Milk with Omega-3	X	6.27
15	2% Milk with Omega-3	X	6.43
22	2% Milk with Omega-3	X	6.61
22	2% Milk with Omega-3	X	5.80

29	2% Milk with Omega-3	X	5.23
29	2% Milk with Omega-3	X	5.34
36	2% Milk with Omega-3	X	5.58
36	2% Milk with Omega-3	X	4.97
0	2% Milk with Omega-3	Y	23.75
0	2% Milk with Omega-3	Y	23.67
1	2% Milk with Omega-3	Y	21.05
1	2% Milk with Omega-3	Y	21.09
3	2% Milk with Omega-3	Y	18.77
3	2% Milk with Omega-3	Y	19.04
8	2% Milk with Omega-3	Y	16.33
8	2% Milk with Omega-3	Y	18.88
15	2% Milk with Omega-3	Y	10.49
15	2% Milk with Omega-3	Y	14.51
22	2% Milk with Omega-3	Y	9.53
22	2% Milk with Omega-3	Y	9.65
29	2% Milk with Omega-3	Y	11.75
29	2% Milk with Omega-3	Y	11.87
36	2% Milk with Omega-3	Y	8.16
36	2% Milk with Omega-3	Y	9.80
0	2% Milk with Omega-3	Z	23.75
0	2% Milk with Omega-3	Z	23.67
1	2% Milk with Omega-3	Z	21.49
1	2% Milk with Omega-3	Z	21.19
3	2% Milk with Omega-3	Z	20.88
3	2% Milk with Omega-3	Z	21.39
8	2% Milk with Omega-3	Z	18.79
8	2% Milk with Omega-3	Z	19.05
15	2% Milk with Omega-3	Z	16.69
15	2% Milk with Omega-3	Z	15.86
22	2% Milk with Omega-3	Z	15.84
22	2% Milk with Omega-3	Z	14.93
29	2% Milk with Omega-3	Z	16.07
29	2% Milk with Omega-3	Z	13.87
36	2% Milk with Omega-3	Z	13.70
36	2% Milk with Omega-3	Z	13.85

Utilizing the integrated rate expression provided in Example 1, the pseudo-first order rate constant (k') of riboflavin degradation was calculated from the data in Table 4 for each bottle code/milk product combination. The R^2 values obtained from the linear regression analyses ranged from 46% to 91%, values which are notably lower than those obtained from the method of Example 10 most likely due to the complexity of the milk product and the steps required to prepare the milk sample for analysis. The resulting k' and R^2 values are provided in Table 5.

Table 5. Riboflavin k' for Milk Products Under Retail Storage Conditions.

Milk Product	Bottle Code	k' (day^{-1})	R^2 (%)
2% Milk	X	0.0286	84.4

2% Milk	Y	0.0095	67.4
2% Milk	Z	0.0074	46.4
2% Milk	F	0.0024	44.7
2% Milk with Omega-3	X	0.0419	84.3
2% Milk with Omega-3	Y	0.0255	84.0
2% Milk with Omega-3	Z	0.0140	90.6
2% Milk with Omega-3	F	0.0090	81.2

The k' data contained within Table 5 of the current Example was compared to those contained within Table 3 of Example 10. Said comparison revealed a linear relationship between the two sets of data for both milk products (2% milk product, R^2 = 92%; 2% milk product with omega-3, R^2 = 100%).

Thus, it can be seen that the accelerated light exposure testing method described in Example 10, which makes use of a simple aqueous riboflavin solution and takes only a few hours per sample to complete, can be advantageously used in lieu of the much more involved light exposure testing method described in the current Example to predict the long term (30+ days) light exposure behavior of a riboflavin containing, complex food system (milk) that is kept in a real world packaging environment (HDPE bottle) under real world storage conditions (lighted, refrigerated storage case).

Example 12.

At pre-determined times during the long term exposure study described in Example 11, for each of the eight sample bottle groups, six bottles were simultaneously and randomly removed from the storage case and their contents combined to form a homogenous mixture. Approximately 3 hours later, the resulting eight mixtures (which were stored until use in one-fluid ounce portions in ice filled coolers that were kept in a 4 ^{o}C walk-in refrigerator) were presented to a group of human subjects (individual appraisers) for evaluation of their sensory properties using standard triangle testing methodology (e.g., ASTM E1885-04, Standard Test Method for Sensory Analysis – Triangle Test). Also evaluated at the same light exposure time points were mixtures derived from two additional sample bottle groups. These latter two groups were produced and stored

as described in Example 11 (one group was associated with the 2% milk product and the other with the 2% milk product fortified with omega-3 fatty acids) but made use of unpigmented, HDPE bottles that were not wrapped in aluminum foil (40.7% average TAPPI opacity, bottle code 'C'). Table 6 provides the bottle code paired comparisons that were studied for each milk product along with the storage times at which the sensory evaluations were performed and the resulting sensory evaluation response data (total responses and correct responses). Also provided in Table 6 are associated 'Correct Response Proportion' values, denoted in this study as R, which were calculated by dividing the number of correct appraiser responses by the total number of appraiser responses.

Table 6. Aggregated Sensory Evaluation Data

Milk Product	Bottle Code Paired Comparison	Storage Time (days)	Appraiser Responses		
			Total (#)	Correct (#)	Correct Response Proportion Values, R
2% Milk with Omega-3	F:C	1	25	15	0.60
2% Milk with Omega-3	F:X	1	25	12	0.48
2% Milk with Omega-3	F:Y	1	24	13	0.54
2% Milk with Omega-3	F:Z	1	24	17	0.71
2% Milk with Omega-3	F:C	3	28	18	0.64
2% Milk with Omega-3	F:X	3	27	10	0.37
2% Milk with Omega-3	F:Y	3	27	12	0.44
2% Milk with Omega-3	F:Z	3	26	8	0.31
2% Milk with Omega-3	F:C	7	34	24	0.71
2% Milk with Omega-3	F:X	7	35	21	0.60
2% Milk with Omega-3	F:Y	7	36	19	0.53
2% Milk with Omega-3	F:Z	7	36	11	0.31
2% Milk with Omega-3	F:C	14	39	34	0.87
2% Milk with Omega-3	F:X	14	38	21	0.55
2% Milk with Omega-3	F:Y	14	36	22	0.61
2% Milk with Omega-3	F:Z	14	38	21	0.55
2% Milk with Omega-3	F:C	21	35	29	0.83
2% Milk with Omega-3	F:X	21	35	30	0.86
2% Milk with Omega-3	F:Y	21	34	30	0.88
2% Milk with Omega-3	F:Z	21	34	15	0.44
2% Milk with Omega-3	F:C	28	35	28	0.80
2% Milk with Omega-3	F:X	28	35	30	0.86
2% Milk with Omega-3	F:Y	28	35	30	0.86
2% Milk with Omega-3	F:Z	28	34	20	0.59
2% Milk	F:C	1	28	11	0.39
2% Milk	F:X	1	28	13	0.46
2% Milk	F:Y	1	26	12	0.46
2% Milk	F:Z	1	25	7	0.28
2% Milk	F:C	3	28	19	0.68
2% Milk	F:X	3	27	13	0.48
2% Milk	F:Y	3	31	18	0.58
2% Milk	F:Z	3	29	12	0.41
2% Milk	F:C	8	35	28	0.80
2% Milk	F:X	8	34	15	0.44
2% Milk	F:Y	8	34	18	0.53
2% Milk	F:Z	8	35	19	0.54
2% Milk	F:C	15	39	30	0.77
2% Milk	F:X	15	38	31	0.82

2% Milk	F:Y	15	38	20	0.53
2% Milk	F:Z	15	38	16	0.42
2% Milk	F:C	22	36	30	0.83
2% Milk	F:X	22	36	26	0.72
2% Milk	F:Y	22	36	22	0.61
2% Milk	F:Z	22	35	14	0.40
2% Milk	F:C	29	37	29	0.78
2% Milk	F:X	29	38	33	0.87
2% Milk	F:Y	29	38	30	0.79
2% Milk	F:Z	29	38	17	0.45

Modeling of sensory data can provide a useful means to estimate parameters such as the sensory shelf-life of a food system (e.g., Hough and Garitta (G. Hough, L. Garitta, Journal of Sensory Studies, 27 (2012) 137-147).

Inspection of Table 6 reveals a time dependence for the calculated R values, denoted as R(t). The R(t) data was modeled (non-linear regression) for all of the milk product/bottle code paired comparison combinations that were evaluated using the logistic growth equation $R(t) = A + (B - A) / \{ 1 + \exp[(t - C) / D] \}$, where t represents exposure time and A, B, C and D are constants which can be characterized within the context of this triangle test study as follows:

A: This constant represents the fraction of appraisers who can correctly discriminate among the different sample bottle codes for a given milk product at extended exposure times. It should be noted that not all appraisers are capable of providing such discrimination, and, as such, the value of this constant is typically below its theoretical maximum of 1.00. The value of this constant is generally influenced by the population of appraisers and the product being evaluated for its sensory properties.

B: This constant represents the fraction of appraisers who can correctly discriminate among the different sample bottle codes for a given milk product at early exposure times. It should be noted that during the early stages of an exposure study such as this one, differences among the sample bottle groups being evaluated are usually not evident except to the most highly discriminating appraisers. As such, this constant (using triangle test methodology) is typically not far from the 0.33 value associated with chance guessing. The value of this constant is also

generally influenced by the population of appraisers and the product being evaluated for its sensory properties.

C: This constant, the value of which is generally influenced by package type (milk bottle in the case of this study) as well as by product type and package storage time and conditions, represents the exposure time at which the R(t) function inflects or, put differently, transitions from the exposure time discrimination region defined by constant B (early exposure times) to that defined by constant A (extended exposure times). For the purposes of this study, we denote said time (i.e. C) as a Sensory Shelf Life (SSL) and use it as the metric by which the light protection performances of the sample bottles evaluated in this study are quantified. Note that increasing SSL values imply increasing light protection capability for a particular bottle type or, put differently, imply that longer sample bottle storage times are required before a majority of the appraisers participating in this study can correctly distinguish the sensory difference between a given experimental bottle and that of an aluminum foil wrapped control bottle.

D: This constant provides a measure of how sharp the transition is through the R(t) function inflection point. The value of this constant is also generally influenced by package type (milk bottle in the case of this study) as well as package storage time and conditions.

Table 7 lists the SSL data derived from the logistic growth function modeling of the time dependent 'Correct Response Proportion' data given in Table 6.

Table 7. Sensory Shelf Life (SSL) Data

Milk Product	Bottle Codes for Paired Comparison	SSL (days)
2% Milk	F:C	3
	F:X	13
	F:Y	25
	F:Z	30+*
2% Milk with Omega-3	F:C	1

	F:X	7
	F:Y	9
	F:Z	28

Notes: *Inspection of the data from this milk product/paired comparison combination showed that the transition to the extended exposure time discrimination region occurred at a light exposure time point that was greater than the 30 days of the exposure study.

The X, Y, and Z plaque derived k' data contained within Table 3 of Example 10 were converted to their corresponding half-lives ($t_{½} = \ln 2 / k'$). These were compared to the corresponding SSL data contained within Table 7 of the current Example (plaque ⇔ paired comparison: X ⇔ F:X, Y ⇔ F:Y and Z ⇔ F:Z). Said comparison revealed a linear relationship between the two sets of data for both milk products (2% milk product, R^2 = 100%; 2% milk product with omega-3, R^2 = 96%).

Thus, it can be seen that the accelerated light exposure testing method described in Example 10, which makes use of a simple aqueous riboflavin solution and takes only a few hours per sample to complete, can be advantageously used in lieu of the much more involved light exposure testing method described in the current Example to predict the long term (30+ days) sensory performance behavior of a riboflavin containing, complex food system (milk) that is kept in a real world packaging environment (HDPE bottle) under real world storage conditions (lighted, refrigerated storage case).

CLAIMS

What is claimed is:

1. A method for producing a packaging design comprising:

(a) providing a known homogeneous liquid sample comprising one or more known photosensitive entities at appropriate concentrations;

(b) providing a cell having controlled optical properties to contain the sample at a controlled temperature between about -20°C and about 100°C;

(c) providing a light source that generates a light beam with a controlled spectral signature between about 290 and about 1000 nm and a controlled intensity between about 0.01 and about 5 W/cm^2;

(d) placing the sample into the cell, rendering a sample cell;

(e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative property;

(f) exposing the shielded sample cell to one or more light beam intensities for one or more durations;

(g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points;

(h) using the data points to determine a photoprotective performance value of the first test material;

(i) repeating steps (a)-(h) with one or more additional test materials under the same conditions to generate one or more additional photoprotective performance values;

(j) utilizing the two or more photoprotective performance values, more preferably more than two, to generate a model for a class of materials that relates that known qualitative or quantitative property to the photoprotective performance;

(k) using the model of step (j) to identify a photoprotective performance value of a packaging material; and

(l) using the packaging material in step (k) to design a package.

2. A method for predicting the photoprotective performance of a material, the method comprising:

(a) providing a known homogeneous liquid sample comprising one or more known photosensitive entities at appropriate concentrations;

(b) providing a cell having controlled optical properties to contain the sample at a controlled temperature between about -20°C and about 100°C;

(c) providing a light source that generates a light beam with a controlled spectral signature between about 290 and about 1000 nm and a controlled intensity between about 0.01 and about 5 W/cm^2;

(d) placing the sample into the cell, rendering a sample cell;

(e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative property;

(f) exposing the shielded sample cell to one or more light beam intensities for one or more durations;

(g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points;

(h) using the data points to determine a photoprotective performance value of the first test material;

(i) repeating steps (a)-(h) with one or more additional test materials under the same conditions to generate one or more additional photoprotective performance values;

(j) utilizing the two or more photoprotective performance values, more preferably more than two, to generate a model for a class of materials that relates that known qualitative or quantitative property to the photoprotective performance; and

(k) using the model of step (j), for materials of the same class, predicting the unknown qualitative or quantitative property of a material based upon a known photoprotective performance value or predicting an unknown photoprotective performance value based upon a known qualitative or quantitative property of the material.

3. The method of Claim 2 further comprising the step:

(l) optionally using one or more values from step (h) or one or more models of step (j) to create a library of data which includes the photoprotective performance values as well one or more values describing the qualitative or quantitative properties of the material;

4. The method of Claim 3 further comprising the step:

(m) optionally using the library from step (l) to identify, describe, and/or predict properties of materials.

5. The method of claim 2, wherein the quantitative or qualitative property comprises one or more of the following : whiteness index ASTM E313; brightness index ASTM D985; CIE L*a*b* tri-stimulus data ASTM designation of E313 -10, D2244, E 1347, E1349, E1477, E2214, E284,

E308, E805, E991, E1331, E275, D2616, D2745, D3134, D3964, D4877, D6290; DuPont Appearance Analyzer data; Diffuse Brightness of Paper and Paperboard (d/0) ASTM D2470; Standard test for haze for plastics ASTM D1003; Brightness, Directional (TAPPI) (T452); Brightness Directional; Brightness, Diffuse (T525); Brightness with Color (Diffuse(Micro TB1C) or Directional/ TAPPI(MicroS-5)); Printing & calculated TAPPI Opacity, Scattering & Absorption Coefficients, Sheet Brightness (T519); Directional / TAPPI Opacity, Scattering Coefficient, Absorption Coefficient (T425); T/dyne Micro TB-1C: Diffuse brightness, opacity, color, color difference, ASTM Index, & tristimulus; T/dyne Micro S-5 BOC:Dir/TAPPI brightness, opacity, color, color difference, ASTM Index, & tristimulus; Color, Hunter or CIE L*A*B* (State Directional or Diffuse Values), opacifying agent composition(s), and/or opacifying agent(s) loading as a design parameter.

6. The method of claim 2, wherein the predictive models are used to facilitate the design of packages that provide targeted photoprotection appropriate for the package contents.

7. The method of claim 6, wherein the package contents include food, beverages, drugs, pharmaceuticals, and/or other photosensitive products.

8. The method of claim 2, wherein the predictive models are used to assess sustainability metrics for a package design.

9. The method of claim 2, wherein the method further comprises correlating the changes to the one or more photosensitive entities in step (g) with one or more sensory evaluation criteria values and utilizing said predicted photoprotective performance to further predict one or more sensory evaluation criteria values of an untested material.

10. The method of claim 2, wherein the sample is maintained under controlled atmosphere conditions.

11. The method of claim 2, wherein the measuring of step (g) comprises evaluating the changes to the one or more photosensitive entities while the sample is contained within the cell.

12. The method of claim 2, wherein the measuring of step (g) comprises removing a sample from the cell and evaluating the changes to the one or more photosensitive entities externally.

13. The method of claim 2, wherein the one or more photosensitive entities are constituents of food, beverages, drugs, pharmaceuticals, or other photosensitive products.

14. The method of claim 2, wherein said sample comprises one or more photosensitive entities selected from one or more of the following classes:

i. natural and synthetic food additives, dyes, and pigments;
ii. chlorophyll;
iii. myoglobin, oxymyoglobin, and other hemeproteins;
iv. water and fat soluble essential nutrients, minerals, and vitamins;
v. food components containing fatty acids;
vi. oils;
vii. proteins;
viii. pharmaceutical compounds;
ix. personal care and cosmetic formulation compounds;
x. household chemicals and their components; and
xi. agricultural chemicals and their components.

15. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from two or more of the classes.

16. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from three or more of the classes.

17. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from four or more of the classes.

18. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from five or more of the classes.

19. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from six or more of the classes.

20. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from seven or more of the classes.

21. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from eight or more of the classes.

22. The method of claim 14 wherein said sample comprises one or more photosensitive entities selected from nine or more of the classes.

23. The method of claim 14, wherein said sample comprises one or more photosensitive entities selected from ten or more of the classes.

24. The method of claim 2, wherein said measuring comprises a test method selected from the group consisting of HPLC, GC, IR spectroscopy, NMR spectroscopy, UV-VIS spectroscopy, GC-MS, LC-MS, fluorescence spectroscopy, ion chromatography, thin layer chromatography, analytical wet chemistry, and electrochemical analysis.

25. A method for predicting the photoprotective performance of a package material for a liquid milk product, the method comprising:

(a) providing a sample comprising an aqueous solution of riboflavin at about 30 ppm and test materials derived from a series of HDPE packages with differing loadings of titanium dioxide;

(b) utilizing the method of Claim 2 to generate riboflavin degradation rate constant data for each test material;

(c) exposing a liquid milk product in test packages constructed of the test materials described in (a) to retail storage conditions and measuring the riboflavin content of said product for each test package as a function of exposure time;

(d) reducing the data from (c) to a riboflavin degradation rate constant for each test package;

(e) relating the rate constant values from step (b) to the rate constant values from step (d) to develop a functional correlation;

(f) testing a packaging test material comprised of HDPE and TiO2 using steps (a) and (b) and applying the obtained data to the model of step (e) to predict the photoprotective performance under retail storage conditions of a package comprised of the test material and containing the given liquid milk product.

26. The method of claim 25 where the time required to obtain predictive photoprotective performance data of a package under retail storage conditions is accelerated by at least 100 times.

27. A method for predicting the photoprotective performance of a material, the method comprising:

(a) providing a known homogeneous liquid sample comprising one or more known photosensitive entities at appropriate concentrations;

(b) providing a cell having controlled optical properties to contain the sample at a controlled temperature between about -20°C and about 100°C;

(c) providing a light source that generates a light beam with a controlled spectral signature between about 290 and about 1000 nm and a controlled intensity between about 0.01 and about 5 W/cm^2;

(d) placing the sample into the cell, rendering a sample cell;

(e) placing a first test material between the light source and the sample cell, rendering a shielded sample cell, wherein the light beam impinges upon the first test material and any penetrating light impinges upon the sample cell, and wherein the first test material comprises a known quantitative or qualitative property;

(f) exposing the shielded sample cell to one or more light beam intensities for one or more durations;

(g) measuring the changes to the one or more photosensitive entities contained within the shielded sample cell at one or more durations to generate data points;

(h) using the data points to determine a photoprotective performance value of the first test material;

(i) repeating steps (a)-(h) with one or more additional test materials under the same conditions to generate one or more additional photoprotective performance values;

(j) utilizing the two or more photoprotective performance values, more preferably more than two, to generate a model for a class of materials that relates that known qualitative or quantitative property to the photoprotective performance; and

(k) using the model of step (j), to identify a photoprotective p erformance value of a packaging material.

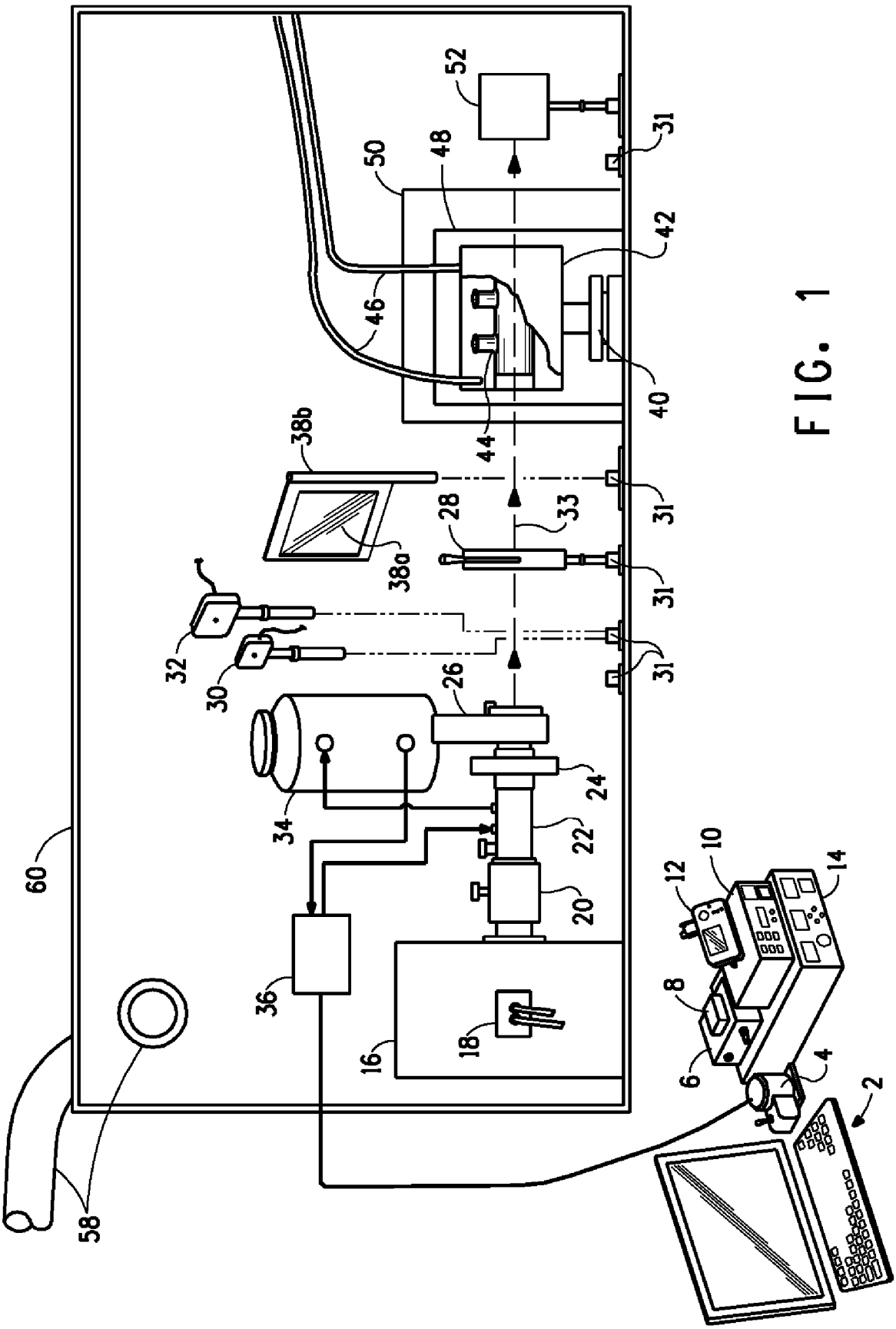
52
31
50
48
42
46
40
44
38b
28
33
38a
32
30
26
24
34
22
20
36
16
18
60
58
12
10
14
8
6
4
2

FIG. 1

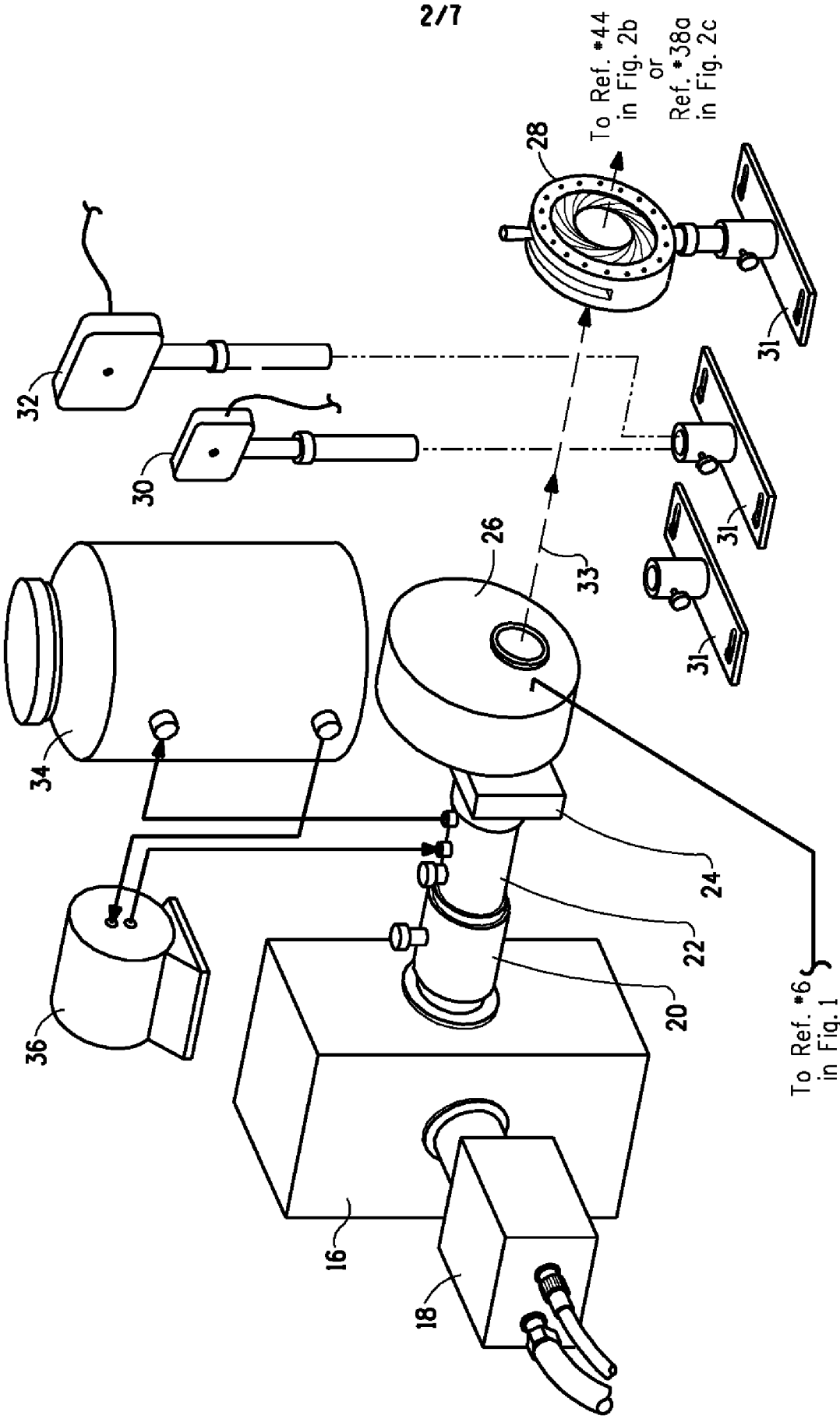
To Ref. *44 in Fig. 2b or Ref. *38a in Fig. 2c
28
31
32
30
31
31
26
33
7
34
24
22
20
36
To Ref. *6 in Fig. 1
16
18

FIG. 2a

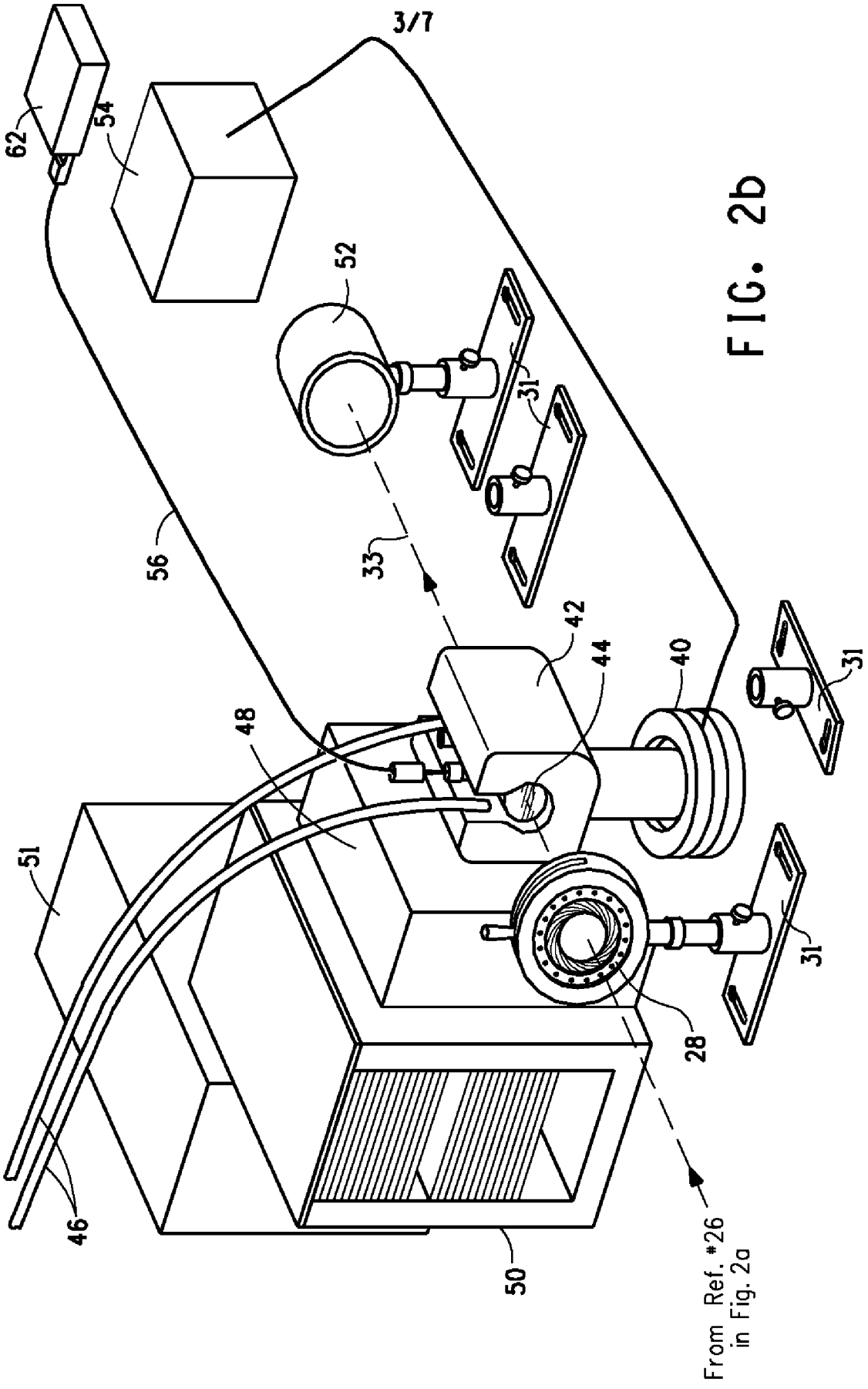

FIG. 2b

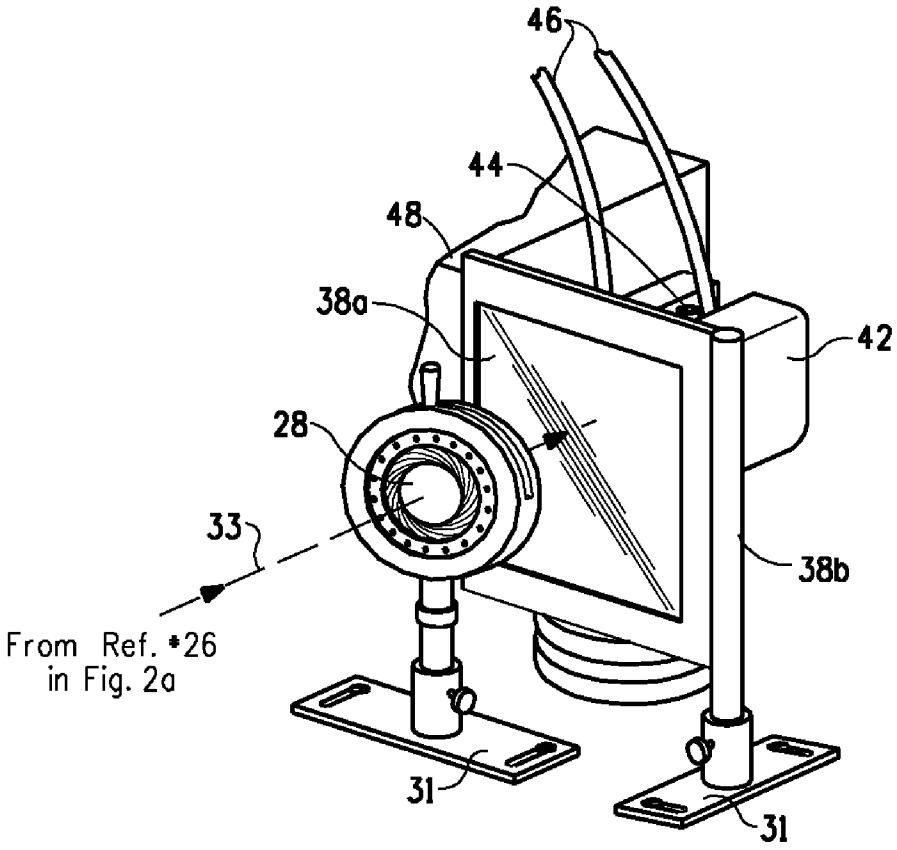

FIG. 2c

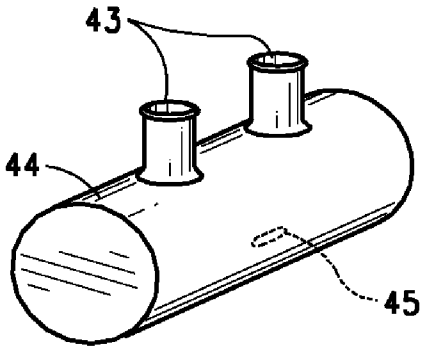

FIG. 3

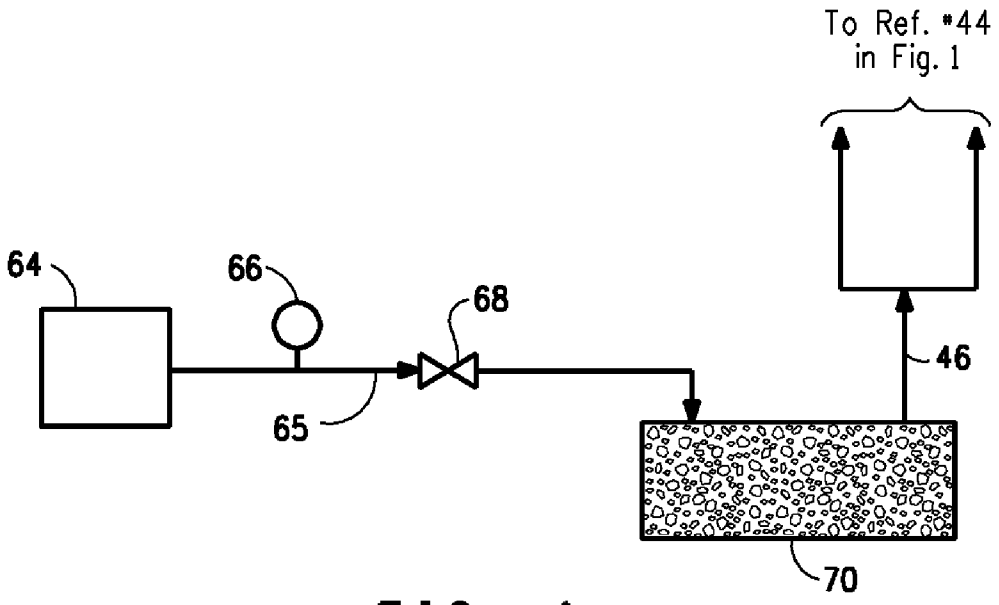

FIG. 4

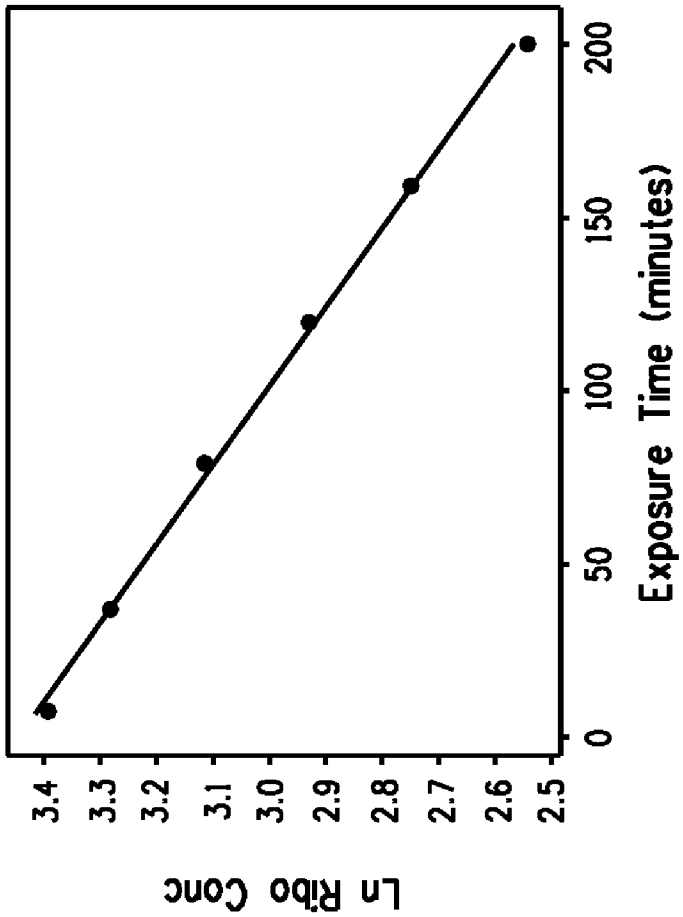
Ln Ribo Conc
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
0
50
100
150
200
Exposure Time (minutes)

FIG. 5

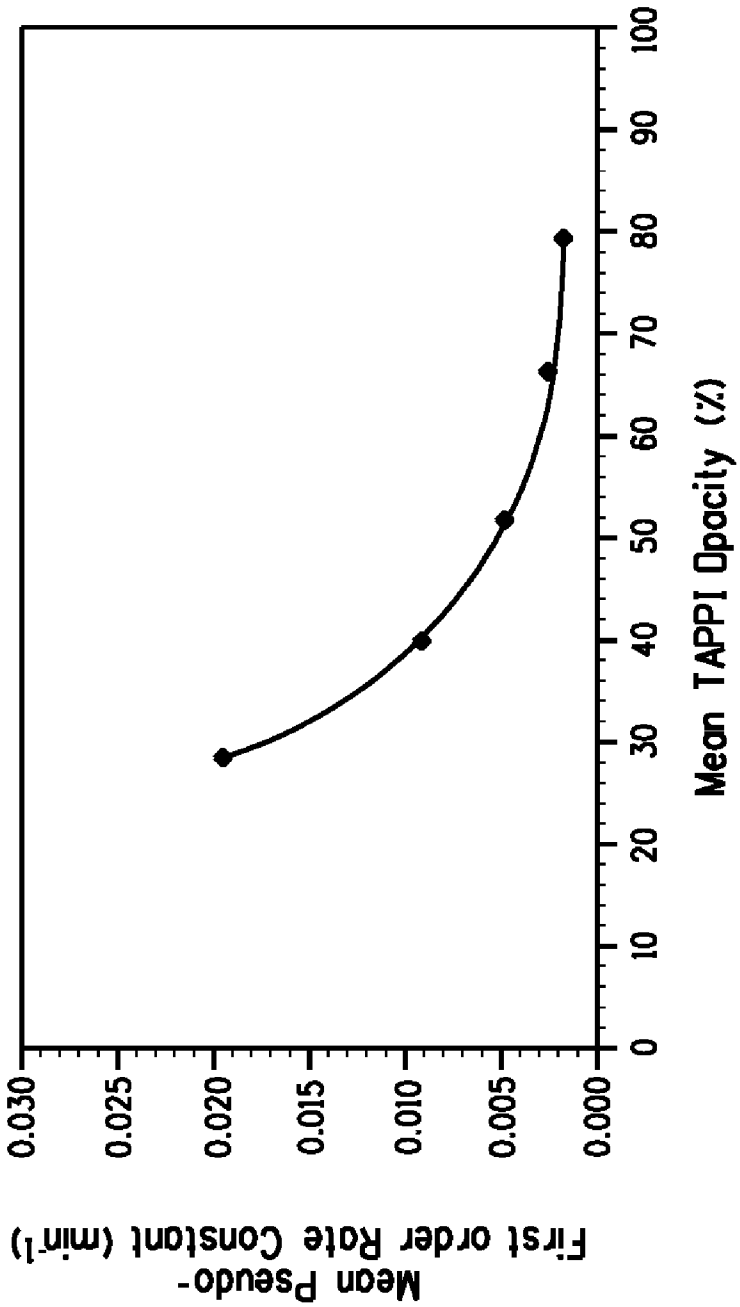
Mean Pseudo-
First order Rate Constant (min-1)
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
10
20
30
40
50
60
70
80
90
100
Mean TAPPI Opacity (%)

FIG. 6