The Intelligent Colorimetric Timer Indicator Systems to develop label Packaging Industry in Egypt

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Abstract:
Attention to the food packaging has become a radical with the need to look for non-traditional packaging solutions. Therefore, this need arises to search for tools to achieve sustainability, particularly in the label technology field. Accordingly, this paper addresses the service as of the tools that help achieving development thru the colorimetric label indicator system manufacturing processes, inks and types of those systems and its application in many packaging fields especially in food and medicine. These considered solutions and systems which are courtesy of corporations are performed on environment and atmosphere friendly label and the development treatments that are made on the products using chemical and physical interactions and its effects on the printed label colorimetric characteristics. Hence, the validation of the paper problem is to bring attention to the new colorimetric indicator systems as one of the most recent label packaging solutions that will help to achieve development the Egyptian packaging market, the importance of the paper is to confirm the proposed indicator label manufacturing, how it can save millions of people lives and the best of them to use. The paper aimed to determine the potential optimization of using timer label in different fields of packaging in Egyptian market to conform to the international market.

Keywords:

Introduction
There is a series of packaging solutions which enable customers across all of the market segments to meet the unquestionable demand for packaging which both informs consumers about the quality and freshness of products, in consumers goods this will primarily help remind shoppers when a pack was opened by providing a clear “consume within” timer. The market for advanced sensor technologies for products packaging is a robust one, as consumers and companies can see value in leaning examining products freshness. These sensors are a natural fit for printing, as smart packaging utilizing color changing inks and pigments can show that the status of a product. We should study within Egypt the new ways to avoid a lot of self-accidents, which has been appear today as a part of our lives and we know this problem as the following name “people deal with packaging products without notice anything” The paper shows how people can save their lives within the new intelligent packaging technologies? The research problem lies on lack of appliance the colorimetric timer labels in Egyptian packaging market, and determination sustainability of this type of label in the market. The research aim to determine the potential optimization of using timer label in different fields of packaging in Egyptian market to conform to the international market.

Methodology:
This study is based on analytical descriptive researches in order to describe and analyze the timer label technology in packaging field.

1. Mono-Color Self Expiring labels
1.1 Self - Expiring for medications
Self-Expiring is a packaging material for medicinal products that visually ‘self expires’ over a fixed period of time. This packaging will graphically display a ‘not fit for consumption’ message using universally accepted danger signs in regional languages. This solution will prevent illegal sales of expired medicines and fatalities arising from their consumption. Consumption of expired medications can lead to prolonged illness, increased healthcare costs, and life-threatening situations. The current solution
of imprinting the expiration date on medicinal packaging is ineffective for multiple reasons including non-universal choice of language (such as English or Arabic), small and unreadable font type, and loss of information with usage or wear and tear. All of these issues can collectively lead to accidental consumption of expired medicines.

The proposed solution uses a packaging material that will visually ‘self-expire’ over a designated time period. The packaging is composed of two layers of information: the foreground, which contains the medicine label, and the background, which carries a hidden expiration message. These are separated by multiple sheets of diffusible material through which the ink from the hidden message will seep through as time passes. This timing sequence will be initiated from the very point of packaging of the medication itself. It will prevent retailers from illegally selling expired medications for personal gains.

The choice of colors and the design of the expiration pattern include universally accepted signs of danger. The ability of the packaging to alert a user visually takes a significant burden off the users. With this solution, the users would not have to struggle with reading fine print in a language they do not understand, or search for a printed expiration date around the packaging with limited visual capabilities and/or dexterity. This solution will prove to be more efficient and widely understood by the illiterate to prevent accidents and fatalities arising from the consumption of expired medicines.

1.2 The Fresh Label: Food Label Changes Color As Food Ages

Another way of self-expiry, the label changes colors based on the level of ammonia the food emits as it ages. After it has passed its expiration date the barcode is no longer readable, making it impossible to sell the product.

The label has one layer of information for the food with the barcode, and another on top with special ink reactive to ammonia; the ink is made of non-toxic, pigment of purple cabbages. Once the meat (or other perishable product) has reached its deadline, the label will change from white to blue, making the product does not pass through the scanner. Once past its expiration date, bar code and unreadable, making it impossible to sell.

“False labeling on food is a worldwide concern. Many consumers carefully check the food labels. However, expiry dates typed on the labels in characters are easily faked and there is a limit for its reliability.

To solve such problem, we can suggest a food label which changes its color by reacting to ammonia given off by food when it is becoming spoiled. When the food is no longer edible, the food label makes a bar code non-scannable and non-purchasable with pattern. This food label is reliable and difficult to counterfeit since it directly reflects freshness.

An hour glass, which is a symbol of time, is chosen as a motif to let consumers intuitively know the freshness. The fresh label will create a new relationship between consumers and food through visualization of ‘Freshness’ which used to be difficult to be shown by the existing food labels.

The fresh label has an award program organized by the Japan Institute of Design that evaluates and encourages unique design, was To-Genko company proposed new method of tracking food expiration dates with the use of a visual aid dubbed The Fresh label.

Over 2,000 items ranging from consumer electronics, automobiles and furniture to office equipment, building designs and sporting goods were exhibited at Tokyo Good Design Expo.
1.2.1 Technology of Insignia LTD

Insignia Technologies has launched a new smart intelligent freshness label aimed at improving customer confidence in the quality of their food while cutting down on unnecessary waste. Easily incorporated into any film lid, the Embedded Timer label is activated when a packet is opened and triggers a timer that changes color as the food within loses freshness meaning hungry fridge-raiders can tell straight away if their snack is out of date or not. With so much food tossed out by would-be consumers after letting a product sit in the fridge too long, Insignia Technologies hopes the innovative new packaging design will help reduce the environmental and economic impact associated with wasted food.

The product changes color when exposed to external influences such as oxygen “variety of gases”, volatiles, UV light and humidity levels, the first generation of this technology starts with light yellow and when CO2 activated it turns dark purple.

Insignia Technologies’ intelligent plastics allow the company to make fully automated timers that can be set to time out within time frames ranging from a few minutes, up to several months. Its major products at the moment are the embedded timer, a stand-alone timer and daily timers, with a range of longer-term timers currently in the final stages of development.

1.2.1.1 Embedded Label

An innovative label which is easily incorporated into a film lid, the embedded label is activated when the consumers opens the packet and triggers a timer to show a strong color change as the food within loses freshness. The embedded timer is the result of a series of technological innovations, leading to the creation of an intelligent label.

1.2.1.2 CO2 INDICATOR PIGMENT

A smart pigment for use in plastic packaging which shows a clear color change when packaging has been damaged for products packed in a modified atmosphere. This allows manufacturers and retailers to remove this product from the supply chain before it even reaches the supermarket shelf.

The intelligent smart pigments can be easily incorporated into plastic food packaging, creating color changing plastic film which will help minimize food wastage and ensure consumers know when food is fit for consumption.

1.2.2 Technology of Freshpoint

1.2.2.1 Oxygen Sensors Technology

O2Sense is a range of patent pending oxygen sensing products aimed at the Modified Atmosphere Packaging (MAP) market. This range consists of 2 primary versions:

1 – An eye readable indicator that gives a clear, visual indication by means of a color change as to whether the amount of oxygen that is present in a sealed food package is within the specied limits. -is indicator is intended to alert producers, retailers and consumers of...
possible breaches of integrity in the package that could lead to an unsafe product.

2 – A machine readable indicator that elicits a clear electronic signal when read by means of a proprietary optical reader that is placed on a production packaging line. It is intended to be used as a quality assurance tool for producers to ensure that the products they manufacture are packaged with the correct level of oxygen.

**Product Status: Under Development**

**Application:**

Both the machine readable and the eye readable versions are intended for use on products in which an incorrect amount of oxygen within the sealed package could lead to a loss of sensory quality and/or a potentially unsafe product to consume. It includes a wide range of categories such as meat, ready to eat meals, dairy products etc.

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**1.2.2.2 DueDropTM Technology**

DueDropTM is a visual indicator that clearly signals the end of the product’s secondary shelf life, encouraging consumers to use the product at its best, and designed to stimulate re-purchase when the product is determined to have expired. DueDropTM indicators take the form of self-adhesive labels, with size and design adjustable to suit the product it is applied to. The active indicator can be calibrated to accurately cover a variety of shelf lives ranging from a few days to years (at room temperature).

![Figure 5: DueDropTM Technology (Courtesy of Freshpoint)](image)

**1.2.2.3 CoolVu Technology**

CoolVu labels are time-temperature indicators that are based on a temperature dependent dissolution (etching) process of a fine aluminum layer. The CoolVu time-temperature indicators arrive as two separate labels of which one consist of a printed aluminum label while the other is a transparent label bearing the etchant in its adhesive layer. The activation of the label is achieved by adhering the adhesive label to the surface of the aluminum label. At the first phase after activation, the aluminum layer becomes thinner as a function of the time and temperature, still preserving its mirror like appearance, Figure 1a. At more advanced stages of the process the active spot turns from being a metallic mirror into black, Figure 1b. Towards the end of its life, the active spot slowly adopts the color that was printed at its backside and at the end of its life the full color of the background is revealed.

![Figure 6: CoolVu labels, a - freshly activated label, b - mid-life label, c - expired label](image)
different pace.

Figure 7: CoolVu labels, a - freshly activated label, b - early mid-life label, c - late mid-life label, d - expired label.

5.2.2.4 BestBy™ Technology
Label is composed of a base substrate, with a clear activator film attached to the top. The secondary shelf life of many food products begins once the primary packaging is opened and/or the seal is broken. BestByTM is a visual indicator that clearly signals the end of the product’s secondary shelf life, encouraging consumers to use the product at its best, and designed to stimulate re-purchase when the product is determined to have expired. BestByTM indicators take the form of self-adhesive labels, with both size and design able to be adjusted to suit the product it is applied to. The active indicator can be calibrated to accurately cover a variety of shelf lives at both refrigerated and room temperature, as determined by the recommended storage conditions of the product after opening.

Figure 8: Before activation Shortly after activation Upon expiry of the product
The label activate by the consumer in 3 steps as following:

Figure 9: Lift cellophane layer Remove inner separating layer Smooth clear film layer back over

1.2.2.5 OnVu™ Technology
OnVu™ indicators can be calibrated to cater for the different spoilage behavior of various foods and beverages. These tailored indicators are highly accurate and consistent in recording and displaying the freshness of the products, based on their time and temperature histories. As the perishable goods are packaged, an OnVu™ TTI is applied and activated using an ultra violet (UV) light source. A filter is then placed over the label to protect it from deliberate or accidental recharging. The label activation and filter placement processes are carried out automatically by a range of OnVu™-capable label dispensers that have been developed to meet industry needs.

Figure 10: OnVu™ indicators (Courtesy of Freshpoint)
1.2.2.6.1 SecQstor Technology
SecQstor is an intelligent label that gives a dynamic and accurate visual indications to the amount of energy that the blood bag it is applied to has absorbed to over a defined period of time. Based on an intelligent technology, SecQstor indicators changes color at rate based on aggregate temperature in which the blood bag is transported and / or stored. This allows for health care professionals and blood banks to manage their inventory of blood products according to the actual temperature history of each individual unit. An intelligent UV trigger mechanism allows SecQstor to be activated and applied to any location.

Figure 11: SecQstor indicators (Courtesy of Freshpoint)

1.2.2.6.2 ONVU Ice Technology
Is a thaw indicator that visually highlights whether the frozen product it is applied to has thawed at any point during its lifetime. OnVu Ice is suitable for a wide range of products. An intelligent UV trigger mechanism allows SecQstor to be activated and applied to any location.

Figure 12: ONVU Ice Technology (Courtesy of Freshpoint)

2- Intelligent Inks
There is many intelligent inks and one of them is Oxygen indicator inks, the group of intelligent ink including: time–temperature, pH, off-gas and food spoiling bacteria indicators, which are being developed at present. As the use of MAP and oxygen scavengers increases and consumers demand more information about the food they eat, especially with regard to its quality and security, so will the demand increase for the overt use of intelligent inks, such as the oxygen indicators described here. Luminescence-based indicators, such as the OxySense “Oxygen Sensor” system, are already being used in food-packaging. Colorimetric sensors, based on simple reversible redox chemistry, such as the Ageless Eye, are also well-established in food packaging. However, these are require storage and handling under anaerobic conditions. Such sensors appear to have great commercial potential and are likely to feature strongly in future smart packaging.

2.1 Colorimetric indicators based on oxygen-binding complexes
It is well known that a differently colored product, oxyhaemoglobin, is formed when deoxyhaemoglobin combines with oxygen. The color change is due to a shift in the porphyrin’s Soret absorption band, from ca. 435 nm to 405 nm, as deoxyhaemoglobin is converted to oxyhaemoglobin. Colorimetric oxygen indicators, consisting of a layer of oxyhaemoglobin, immobilized on an action exchange resin, positioned at the end of a
2.2 Colorimetric redox dye-based indicators
The most commonly-employed leak indicator used in food packaging is a colorimetric redox dye-based indicator, the Ageless Eye produced by the Mitsubishi Gas Company to support its extensive range of Ageless oxygen scavengers. The Ageless Eye oxygen indicator, and other such colorimetric redox dye-based indicators

2.3 Colorimetric light-activated, redox dye-based oxygen indicators
There is several colorimetric, light-activated, oxygen indicators for use with food packaging based on the above riboflavin/EDTA photosystem. riboflavin is highly fluorescent in its oxidized state, and non-fluorescent in its reduced state

2.4 Luminescence-based oxygen indicators
Most optical sensors for oxygen are luminescence-based. In such systems the luminescence associated with an electronically excited lumophore, \( L^* \), is quenched irreversibly by molecular oxygen

\[ L^* + O_2 -> L + O_2^* \]

The luminescent probe molecules are usually encapsulated in a gas permeable, ion-impermeable, material such as silicone rubber, or an organic polymer, such as poly(vinyl chloride), to create thin film, oxygen indicators.

3- Inks developed by VTT (Technical Research Centre of Finland)
They are focused on formulation of the ink, the issues related to the reactive substances contained in the ink, the serviceability of the ink in the printing process, and the compatibility of ink and printing substrates (Plastics, fiber based materials), and the printing used techniques is flexography printing and ink jet printing methods. The color change reaction of the printed and heat activated indicator systems and a water based ink for fibre based substrates and a solvent based ink for plastic substrates were developed. The reactive substance in the indicator is water soluble. In order to prepare a solvent based ink, a derivative of a molecule was prepared. The indicator which designed with this type of ink is to be used on the inner surface of any package. Therefore, food additives or other elements suitable for content with food were used.

The most crucial part in the printing technology is the ink and its physical properties:
- Ink: viscosity, surface tension, non-foaming, non-corrosive, stable, non-toxic, non-bacterial growth.
- Image: good adherence, quick drying, high color density, light and moisture resistant, smear resistant.

Indicator performance: reliable color change, sensitivity, stability during ageing, absence of interfering reactions, reliable operation in various working conditions, humidity and temperatures, irreversibility.

The developed package leakage indicator systems have following features:
- Activated by heating (e.g 121 °C) or by volatile reducing agent.
- All ingredients are food additives or suitable for direct contact with food
- Indicator inks are printable directly on the inner surface of the package, on stickers and on oxygen absorber pouch.
- Three ink products have been developed; water-based for paper substrate, water-based for plastic substrate and solvent-based for plastic, and the both inks have good adherence on plastic and paper.
- Printable in text or code form and use with oxygen absorber
- Adjustable speed of reaction, clear and irreversible color change
- Good sensitivity against visible light and no specific requirements on storage conditions before or after applying indicator in package.

![Figure 13: Demonstration of indicator color change after exposure to oxygen](image)

4- Case Study:
The research was carried out in EU project Nafispack “Natural Antimicrobials For
Innovative and Safe Packaging\textsuperscript{“}, and has received funding from the European Community’s Seventh Framework Program FP7/2007-2013 under grant agreement number 212544 & the development work continues in EU projects SusFoFlex Smart and sustainable food packaging utilizing flexible printed intelligence and materials technologies funded by EU FP7/2007-2013 under grant agreement number 289829.

4.1 Materials and Methods:
The reagents for the indication reaction were incorporated into a system containing solvent, binder and additives. The main ingredients are a reagent and a pH-dye, and the composition can be tuned as for the sensitivity. Two ink formulations were tested in the final storage test. The formulations were applicable by printing. The white carrier paper material helps detection of the color change. The indicators were attached in MA packages of salmon, which were stored in chilled conditions. The fish quality was assessed by gas composition analysis, photography, color measurement, microbiological analyses and chemical analysis of volatile components. The sensory quality characteristics (appearance, odor, texture by hand) at five different times during a period of two weeks were assessed.

4.2 Case study findings:
Acetaldehyde, ethanol, 3-hydroxy-2-butanone (acetone) and isopentyl alcohol were identified as markers of spoilage. The occurrence of these substances seemed to correlate well with the microbial quality of the salmon. Sulphurous or nitrous substances could not be detected in the used experimental setup. The indicator was therefore designed to detect aldehydes and ketones.

The fresh salmon fillet samples in HDPE trays were stored at 4°C for 15 days. Initially, there were no detectable amounts of acetone present in the headspace of the packages. The substance appeared between day 7 and day 12, and during the last days of the storage period the acetone concentrations decreased, possibly due to further degradation. Acetaldehyde was observed in amounts close to the odour threshold already on day 1, and a sharp increase was observed during the last few days of storage. The study on odour, texture and appearance showed that the quality of salmon in packages was good on day 7 but deteriorated on day 12. The total viable counts in salmon fillets increased from 3.40 log cfu/g at the time of packaging to >8 log cfu/g at the end of storage. Relatively high number (7 log cfu/g) was reached after 11-12 days of storage. The results indicate that lactic acid bacteria constituted the major part of the total bacterial count in the salmon fillets. The content of hydrogen sulfide producing bacteria reached a relatively high number (> 5 log cfu/g) after ca. 14 days of storage, followed by a steadily increase to 16 days of storage.

The performance of the two indicators in the storage test was studied using principal-component analysis on indicator color change and microbiological test results, and the results were evaluated observing the sensory and chemical test results. According to the study the expired samples and the non-expired samples were explicitly grouped. Only a small number of samples stored for 12 to 14 days were considered to display an incorrect read-out. A further observation was the softening of the fibrous carrier material during the storage period due to the high moisture content in the fish package.

In this project specific safe substances were selected as ingredients for the indicator. The reaction, originally in liquid phase, was transferred into a solid phase spot on a carrier material detecting minor amounts of analyst. The sensitivity of the indicator can be influenced to some extent by adjusting the formulation.

4.3 Changing colors during test:
The indicator responded to fish spoilage through visible color difference $\Delta E$ from yellow to...
orange-red (first version) and from colorless to red (second version) depending on choice of pH-dye. The spoilage as measured by the microbiological, sensory and chemical methods was detected by the indicators. However, the validation study indicates that the indicator formulation should be adjusted to a more sensitive mode. Further, the moisture resistance should be improved. The indicator can be applied in consumer package systems indicating that the quality of the selected packaged food product has been maintained throughout the distribution chain.

Figure 15: values of color change in rapid spoilage test of indicator 1 & 2

4.4 Author Technical Analysis

1. While the spoilage measured by microbiological, sensory and chemical methods detect by indicators, the used indicator systems aren’t so sensitivity and should be adjusted to be more sensitive.
2. The relation between color difference $\Delta E$ and time of product spoilage can show us the changing of the colors through the time, but adjusting and improving the indicator sensitivity can improving color changing through timing and it should be done to improve clarity of the color changing.
3. Materials and methods were developed while using two different types of ink formulations tested in the study, the result of the performance study of the inks formulation and $\Delta E$ in the two cases shows that the second indicator which changed from the colorless to the red color (Indicator 2) show clarity than the other one though color changing process, and can easily use by the consumer.
4. Some of the indicators aren’t capable to work as spoilage tester and doesn’t show us the spoilage process within the 14 days or any changing of the colors, so we should avoid using those indicators on the packaged products.
5. The color difference value $\Delta E$/time in testing of indicator 2 higher than indicator 1, means that changing indicator colorimetric is higher in indicator 2, also it shows us that the inks formulation and sensitivity in indicator 2 much correct than indicator 1

4- Results:

1. The new intelligent label packaging design will help reducing the environmental and economic impact associated with wasted food.
2. The new launched intelligent timer indicator labeling system aimed to improving customer confidence in the quality of their products like food, medications…. Etc; this type of technologies makes people aware of what they deal with and what the expiry date of the product is.
3. Each new intelligent freshness indicator systems technology has its own ink formulation technology.
4. The intelligent ink has several indicators depending in its working on Oxygen.
5. Timer indicator system labeling will help saving people lives and will reduce its risk.
6. Egyptian people need timer indicator label system as a mean of health insurance on their life
7. Antimicrobial packaging is one of the industry’s latest innovations which will help to reduce spoilage and increase the shelf life of food by inhibiting the growth of bacteria, molds and yeast as well as reduce the risk of contamination from pathogens such as E coli.
8. The higher color difference value $\Delta E$ of the
indicator systems makes them more reliable and trusted than the weakest one, and it will be easy to use by the consumers.

8. Conclusion
1. The intelligent colorimetric timer labeling technologies have a wide range of its indicator systems available for detection of spoil products during packing period.
2. Timer intelligent Freshness label technology in developing packaging success in detect spoil products.
3. Egyptian packaging corporations can develop their own package using Timer intelligent Freshness label technology “the indicator systems”.

Therefore, it is recommended that – Use the indicator systems in the field of packaging and development packaging is to be intensified in Egyptian market to conform to the international market. Also the use of The Timer intelligent Freshness label technologies or the indicator systems in packaging concerned educational institutions should be designed with care.

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