I. INTRODUCTION

Although numerous items in our supply systems, both military and commercial, deteriorate during storage, it is not often that the degree of deterioration is evident to the human senses. An objective method of indicating the rate and extent of deterioration appeared to be feasible, however, since the deterioration of many items is a function of temperature and length of storage. An extensive study on long-term storage of military rations was conducted by the former Quartermaster Food and Container Institute and the University of Georgia (2) for various periods of storage time up to seven years. The experiment consisted of storage and examination of a total of 93 military ration items, in more than 26,000 cans and 86,000 flexible packages. The most outstanding finding was that the storage life of food products was highly dependent on both the length of time and the temperature during the storage period. A typical example was that the maximum storage life of a canned pound cake was determined to be 6 months at 100°F, 2 years at 70°F, or 4 to 5 years at 57°F.

It should be clearly understood that dependence on time and temperature of products in storage is not limited to food items; it encompasses many medicinal products, ammunition, electronic parts, photographic films and numerous other items. Virtually any product which undergoes slow chemical reactions in storage would have strong dependence on time and temperature.

In our military supply system, the length and temperature of storage are sometimes beyond our control. Moreover, most storage areas will show considerable temperature variations, depending on the time of day, season of the year, location of the warehouse and locations within the warehouse. A date on the package will tell how long the product was in storage but will say nothing about the temperature history. A maximum temperature indicator will show peak temperatures but not how long the product has been subjected to the peak temperature or other temperatures. Thus, what is needed is a device which...
can integrate the time-temperature (T-T) exposure history of supply items and provide an output related to product deterioration. Expensive and complicated electronic equipment can give this information but the use of such equipment is precluded in an extensive supply system because of its cost. A simple and inexpensive label or tab which could be attached to each carton and show by a suitable color change, or appearance of a warning message, when the product is approaching the end of its useful life, would have great practical value.

II. THEORETICAL ASPECTS

The rate of O₂ permeation through plastic films generally obeys a simple form of fick's law:

\[ Q = P \frac{A \cdot t \cdot \Delta p}{1} \]

where \( Q \) is the amount of O₂ passing through a film of area, \( A \), and thickness, \( 1 \), for a time, \( t \), with vapor pressure difference across the film of \( \Delta p \), and a permeability constant of the film material, \( P \).

According to the Arrhenius equation, the permeability constant, \( P \), is an exponential function of the absolute temperature \( T \), as expressed by the equation:

\[ P = P_0 e^{\frac{-E}{RT}} \]

where \( P_0 \) is a permeability constant at absolute zero, \( E \) is the energy of activation of the permeation process, and \( R \) is the gas constant. By substituting \( P \) as given in equation (2) into equation (1), we obtain:

\[ Q = P_0 e^{\frac{-E}{RT}} \frac{A \cdot t \cdot \Delta p}{1} \]

In equation (3), it is clearly indicated that the amount of O₂ passing through a film, \( Q \), is directly proportional to time, \( t \), and is an exponential function of the absolute temperature \( T \), when the film area, \( A \), and thickness, \( 1 \), and O₂ vapor pressure difference, \( \Delta p \), are constant. Recalling the storage data of canned pound cake cited in the Introduction Section, an exponential rate of decrease in quality (storage life) in relation to increase of storage temperature was evident. The fact that the storage life of a product, and the amount of O₂ permeating through a film, are both exponential functions of temperature is the theoretical basis of our approach. By inclosing a suitable oxygen-reacting chemical system in a pouch made of plastic films, the extent of reaction which occurs depends upon the amount of oxygen which permeates the film. Since oxygen permeation through a film is time- and temperature-dependent, the extent of reaction is effectively controlled by time and temperature. If the reaction produces a visible change, such as a colored end product, we achieve a color-changing time-temperature indicator. The rate of oxygen permeation and thus the length of time required for the indicator to show change can be adjusted at will by varying the thickness or structure of the plastic material making up the pouch.
The system can be further adjusted by changing the amount of reducing or buffering agents used in the oxygen-reacting chemical system. Thus the end-point of such a T-T indicator can be adjusted so that it will correspond to the end-point of the useful life of a storage item.

III. MATERIALS AND METHODS

A number of oxidizable chemical systems enclosed in a wide variety of plastic pouches were tested and shown to have practical application possibilities. These systems can be divided into the following four groups:

A. Redox dye system.

A number of redox dyes, such as thioindigo and sodium anthraquinone \(\beta\)-sulfonate can develop marked color changes in our plastic pouch system in response to time and temperature in storage. An anthraquinone derivative was used in our test work to convey written messages by means of the color change. It is well known that in dissolving sodium anthraquinone \(\beta\)-sulfonate and sodium hyposulfite in aqueous alkali, a rich blood-red solution is obtained (3). When it is shaken with air, the red color is gradually changed to colorless. Because sodium hyposulfite is unstable in solution during long-term storage, zinc dust was substituted as the reducing agent. The chemistry of this redox system is shown in Figure 1. The color change from a blood-red solution to a practically colorless one due to oxidation was utilized to convey messages. The words "Discard" or "Use Up First" were printed on a filter paper in black letters. This was placed inside a plastic pouch. A quantity of anthraquinone-zinc solution with the blood-red color was added to the pouch which was quickly purged with an inert gas such as \(\text{N}_2\) or \(\text{He}\) and heat-sealed. The black letters written on the filter paper were now covered by the opaque blood-red solution and therefore completely obscured. During storage, \(\text{O}_2\) in the air gradually permeated the pouch at a rate depending on the time and temperature of storage, and oxidized the solution to a colorless form. The hidden letters on the filter paper thus became visible, completing the mechanism for transmitting written messages. In making up one liter of anthraquinone-zinc solution, the following chemicals were used:

- Sodium anthraquinone \(\beta\)-sulfonate 40 gm.
- Zinc dust 96 gm.
- Sodium hydroxide pellets 132 gm.

For an indicator to have practical application value, stability under sunlight and high temperatures is required. This means that the indicator as a chemical entity shall not decompose due to light or thermal effects. Special tests were set up to investigate the effect of light by directly exposing pouch samples filled with anthraquinone-zinc solution to sunlight. The controls were similar samples covered by black papers. For checking thermal effects, similar pouch samples stored in a helium atmosphere were
exposed to a high temperature. In addition, 1 ml quantities of the solution were sealed under helium gas in soft glass capsules. They also were exposed to sunlight and a high temperature for stability studies.

B. Inorganic system.

1. Change of Fe$^{+2}$-Fe$^{+3}$. Ferrous chloride solution which is virtually white was used in a plastic pouch with a white filter paper as the background. On exposure to air, this solution is slowly oxidized with accompanying formation of a ferric solution which is greenish-yellow in color. After the solution has been standing some more, a rusty-brown ferric oxide precipitate is formed. A system using ferrous chloride alone does not have much utility in our application, since color resulting from the presence of ferric ion will begin to form as soon as the first bit of oxygen has reacted. This early appearance of color will occur regardless of the amount of ferrous chloride used in the pouch. Thus long-lasting indicators cannot be made from ferrous chloride alone. However, use can be made of another interesting property of the ferric ion. This ion reacts with phosphate ion (PO$_4^{3-}$) to form a colorless complex. By the use of a judicious amount of phosphoric acid with the ferrous chloride in the pouch, color formation can be delayed. This makes it possible to build time into the indicator with as short or as long an indicating time as we wish. The sequence of reactions occurs as follows:

$$\text{Fe}^{+2} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}^{+3} + e^-$$

$$\text{Fe}^{+3} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 \text{ (colorless)}$$

When all PO$_4^{3-}$ is consumed, excess Fe$^{+3}$ (greenish-yellow color)

$$4\text{Fe}^{+3} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \text{ (rusty-brown)}$$

In carrying out this study, a piece of filter paper was placed in the pouch along with a quantity of FeCl$_2$·H$_2$PO$_4$ solution. The pouch is purged with an inert gas and then heat-sealed immediately. In time, enough oxygen permeates the pouch to complete the color-changing process. In making up one liter of FeCl$_2$·H$_2$PO$_4$ aqueous solution, the following composition was used:

- FeCl$_2$·4H$_2$O: 199.0 g
- H$_3$PO$_4$: 9.8 g

2. Change of Cu$^0$-Cu$^+$. It is a known phenomenon that copper metal (Cu$^0$) dissolves in ammonia to form copper-ammonia complexes in the presence of oxygen (1). If a message written on paper is covered with copper foil and placed in a pouch along with an ammonia solution, the written message will be revealed in time as oxygen permeates the pouch and causes the removal and the solution of
the copper foil with the formation of copper-ammonia complexes. Reactions inside the plastic pouch are as follows:

$$\begin{align*}
\text{Cu}^0 + \text{O}_2 & \rightarrow \text{Cu}^2 + e^- \\
\text{Cu}^+ + \text{O}_2 & \rightarrow \text{Cu}^{2+} + e^- \\
\text{Cu}^+ + 2\text{NH}_3 & \rightarrow \text{Cu(NH}_3)_2^+ \quad \text{(colorless)} \\
\text{Cu}^{2+} + 4\text{NH}_3 & \rightarrow \text{Cu(NH}_3)_4^{2+} \quad \text{(blue)}
\end{align*}$$

In making up one liter of ammonia reagent solution for our experiment, the composition employed was: dissolve 150 g of $\text{NH}_4\text{Cl}$ in water to 500 ml, and add 500 ml of concentrated $\text{NH}_4\text{OH}$ solution (26-30% $\text{NH}_3$).

C. Enzyme system.

It is commonly known that the enzyme glucose oxidase acts in the presence of molecular oxygen to catalyze the following reaction:

$$\text{Glucose} + \text{H}_2\text{O} + \text{O}_2 \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + \text{H}_2\text{O}_2$$

The acidity developed due to the formation of gluconic acid can be easily detected by an acid-base indicator, such as methyl red (color change pH range, 4.2 - 6.3, red-yellow). By using different amounts of buffering agent in the system, the pH developed as a result of the oxidation can be varied. Inclosed in a pouch are solutions of glucose, glucose oxidase, a buffer, a few drops of methyl red, and a strip of filter paper. The formation of gluconic acid in the pouch shifts the pH downward thus causing the included indicator methyl red to turn red (from the original light yellow) which is the end point of the indicator. Solutions used were prepared as follows:

1. Glucose: 2% solution.
2. Glucose oxidase: 100 ml of activity taking up 1 ml $\text{O}_2$/hour at 38°F.
3. Methyl red: 100 mg/100 ml ethyl alcohol.
4. Phosphate buffer: 0.06 molar $\text{KH}_2\text{PO}_4$-$\text{NaOH}$, pH 7.

D. Rubber sheet system.

Rubber oxidizes readily and becomes brittle, especially if it is stretched under stress. It develops transverse cuts which may never he completely. Some chemicals known as antioxidants can retard the oxidation process if added before oxidation starts. These phenomena were used to demonstrate another time-temperature indicating system. Opaque sheets of vulcanized natural rubber were prepared with antioxidant left out according to the formula (5):
Cured 20-25 minutes at 225°F. in the oven, the sheet was about .006 inch thick. A piece of the rubber sheet was stretched across the top of a shallow aluminum cup with edges folded down over the side and held tightly in place with a rubber band. Underneath the opaque rubber sheet was a piece of colored paper or a written message. The mounted cup was placed inside a plastic pouch for storage. When the stretched rubber sheet oxidized, it split apart and revealed the color or message underneath.

IV. RESULTS AND DISCUSSION

Test results are presented in four groups in accordance with the headings used in the "Materials and Methods" section.

A. Redox dye system.

10 ml of supernatent liquid of anthraquinone-zinc solution described in the "Materials and Methods" section, was placed in a pouch, 3-5/8 x 4-3/4 inches. A piece of filter paper with a written message "Discard" was also included in the same pouch. The message word "Discard" was obscured by the opaque blood-red color of the anthraquinone-zinc solution and therefore was invisible. In storage, O2 gradually permeated the pouch and oxidized the solution so that it became colorless. The hidden message ("Discard") on the filter paper thus became visible. Results of the storage at different temperatures are shown in Table 1.

Table 1. Time in days required for the message word "Discard" to appear in the anthraquinone system.

<table>
<thead>
<tr>
<th>Pouch Materials</th>
<th>Storage Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32°F.</td>
</tr>
<tr>
<td>.001 in. Mylar/.002 in. polyethylene</td>
<td>No appearance</td>
</tr>
<tr>
<td>(single pouch)</td>
<td>within 134 days</td>
</tr>
<tr>
<td>Inner pouch: .001 in. Mylar/</td>
<td>No appearance within 134 days</td>
</tr>
<tr>
<td>.002 in. polyethylene</td>
<td></td>
</tr>
<tr>
<td>Outer pouch: .001 in. polyethylene/</td>
<td></td>
</tr>
<tr>
<td>.002 in. Aclar/ .0005 in. Mylar/2.2 lb.</td>
<td></td>
</tr>
<tr>
<td>polyethylene (double pouch)</td>
<td></td>
</tr>
</tbody>
</table>

The storage samples described in Table 1 were photographed and are shown in Figure 3. Results conclusively indicate that
the appearance of the message word is directly responding to both the storage temperature and time in storage.

Extensive tests were made to determine light and thermal effects on the stability of anthraquinone-zinc system. Results are summarized as follows: (1). Pouch samples filled with anthraquinone-zinc solution were directly exposed to sunlight in the summer for 100 days. The controls were similar samples covered by black papers. Results: Test samples and controls were identical in color reaction whether they were directly exposed to sunlight or kept in the dark. (2). For checking thermal effects, pouch samples stored in a helium atmosphere were exposed to high temperature of 130°F. for 100 days. Results: They were not appreciably different from the ones stored in the similar atmosphere but exposed to only 70°F. (3). 1 ml quantities of the solution were sealed under helium gas in soft glass ampoules. They were exposed to the following conditions: 30°F.; 70°F.; directly exposed to the sunlight; outdoors, but kept in the dark; 130°F. room, directly under a sun lamp; 130°F. room, dark. Results: All ampoules showed very little or no color changes under the above test conditions for 120 days. The evidence available indicates that there would be no light or thermal stability problems with an indicator made from anthraquinone-zinc solution. The implication is that this system can be used outdoors as well as indoors.

B. Inorganic system.

1. Change of $\text{Fe}^{++}$-$\text{Fe}^{+++}$. 10 ml of $\text{FeCl}_2\cdot\text{H}_2\text{PO}_4$ solution described in "Materials and Methods" section, along with a piece of filter paper, were placed in a pouch, 3-3/4 x 4 inches. The initial color was virtually white. On oxidation, it changed to greenish-yellow, and then finally to rusty-brown. The appearance of rusty-brown is regarded as the end-point at which the storage item would be considered to be unsatisfactory for its intended use. Results are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Time in days required for the appearance of the rusty-brown color in $\text{FeCl}_2\cdot\text{H}_2\text{PO}_4$ solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pouch Materials</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>.001 in. Mylar/.002 in. polyethylene (single pouch)</td>
</tr>
<tr>
<td>Inner pouch: .001 in. Mylar/.002 in. polyethylene</td>
</tr>
<tr>
<td>Outer pouch: .001 in. polyethylene/.002 in. Aclar/ .00075 in. Mylar/2.2 lb. polyethylene (double pouch)</td>
</tr>
</tbody>
</table>

The samples described in Table 2 were photographed and are shown in Figure 4. Pouch samples of $\text{FeCl}_2\cdot\text{H}_2\text{PO}_4$ were exposed to sunlight, and also to high temperatures under helium atmosphere,
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as was done with the anthraquinone system. Results showed that they were both light- and heat-stable. Basically, there are 3 distinct colors which occur in FeCl₂-H₃PO₄ solution during storage: the initial virtually white color; the intermediate greenish-yellow; and, finally, rusty-brown. If we provide a reference color chart accompanied with written information, a meaningful rotation of storage items may be achieved. One proposed reference color chart with written information is shown in Figure 5. In this proposed system, as long as the indicator remains virtually white and matches the first color chip, the product inside the container is safe for use; when the indicator changes to greenish-yellow and matches the second chip, the product is still good for use but should be rotated and used up as soon as possible; when the indicator finally changes to rusty-brown and matches the third color chip, the product has deteriorated to a stage which makes it unsatisfactory for its intended use and therefore should be discarded.

Another test was set up to show that the time required to observe a color change of the FeCl₂-H₃PO₄ solution would vary with the amount of solution placed in pouches with a given oxygen permeability. The amount of solution placed in each pouch varied from 1 ml, 2 ml, 5 ml, 10 ml, to 20 ml. Pictures in Figure 6 clearly show that the larger the amount of solution in each pouch, the longer the time required for color to change at each storage temperature. This proves conclusively that the color change does depend on: (1) The oxygen-absorbing capability of the solution and amount; and (2) The temperature at which the indicator is stored and (3) The time of examination. With the same amount of solution in a pouch, the color-changing property depends solely on time and temperature.

2. Change of Cu⁰⁻Cu⁺. Results of our testing indicated that the ammonia which was used as the complexing agent for copper permeated the film pouch and was lost to the outside atmosphere very rapidly. For example, in placing 10 ml of ammonia reagent solution as described in the "Materials and Methods" section, in a pouch made of .0005 in. Mylar/.003 in. H/D polyethylene, the permeation rate was 6.8 mg/100 cm²/24 hr at 75°F. (by acid titration). In some instances, ammonia also showed chemical reactions with adhesives ordinarily used in pouch film lamination, thus causing film delamination. Despite these disadvantages, the copper-ammonia system did indicate a unique property as a T-T indicator. After the copper foil was oxidized and dissolved in the presence of ammonia, the appearance of the written message originally covered by the copper foil was striking. Moreover, the copper foil technique offers a possibility of making up a multi-stage indicator by laminating 3 or 4 foils together in a series, each carrying a written message. The successive written messages will appear after each foil dissolves away, thus establishing a multi-warning system for a storage item. Because of the shortcomings of ammonia when used in film pouches, as mentioned above, other complexing agents suitable for copper and yet compatible with film pouch materials will be sought.
C. Enzyme system.

A simple test was set up to examine the validity of the enzyme system. In a 2 x 4 inch polyethylene pouch of .002 in. thickness the following quantities were inclosed along with a piece of filter paper (solution concentrations are listed in the "Materials and Methods" section): glucose 1.0 ml, glucose oxidase 0.5 ml, methyl red 3 drops, and phosphate buffer and water to make up to 2 ml as shown in Table 3.

The initial solution color inside the pouch was light yellow. The glucose was oxidized in the presence of the enzyme glucose oxidase to gluconic acid, causing the solution pH to drift downward, thus, in turn causing the indicator methyl red to turn red.

Table 3. Time required for the appearance of red in the glucose oxidase system inside plastic pouches (at 70°F.).

<table>
<thead>
<tr>
<th>Phosphate Buffer (ml)</th>
<th>Water (ml)</th>
<th>Time for the solution to turn red (Minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.00</td>
<td>10</td>
</tr>
<tr>
<td>0.05</td>
<td>1.95</td>
<td>15</td>
</tr>
<tr>
<td>0.10</td>
<td>1.90</td>
<td>20</td>
</tr>
<tr>
<td>0.50</td>
<td>1.50</td>
<td>60</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>90</td>
</tr>
<tr>
<td>2.00</td>
<td>0</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 3 shows that the lowering of solution pH is directly responding to the amount of buffer solution added. Pouches made of polyethylene have a rapid O₂ diffusion rate, and the enzyme system under study is very sensitive to O₂ concentration. Further testing of glucose oxidase at 100°F. and 130°F. in pouches less permeable by oxygen and for a longer period of time did not show the temperature effects which would be expected due to the increasing oxygen permeability at higher temperatures. Presumably, this result was due to enzyme inactivation by high temperature. The inherent instability of enzymes at higher temperatures casts doubts on the long-lasting property of enzyme system above 100°F. Therefore, it is suggested that this system is best suited for items normally stored at low temperatures, such as frozen or refrigerated products.

D. Rubber sheet system.

To demonstrate the validity of this principle, specially compounded rubber sheets mounted on aluminum cups as described in the "Materials and Methods" section were stored at 130°F. One set of mounted rubber sheets was directly exposed to air, and another kept under helium gas. The mounted rubber sheets exposed to air broke apart within a week, while the ones stored under helium gas showed no sign of breaking during a 1-month storage, as shown in
Figure 2. Although these tests have proven that the rubber sheet system can be adopted for indicating time and temperature effects, mechanical impacts such as dropping, vibration, and rubbing (sometimes unavoidable during the transporting and handling of containers) can also cause the rubber sheet to break prematurely. Therefore, its application to indicating time and temperature storage history is limited to stationary objects. It might be used to monitor conditions inside a warehouse, or in a special storage area.

V. CONCLUSIONS

A. Our original concept of developing T-T (time-temperature) indicating systems which can be related to product deterioration has been established and proven for several possible systems. Our approach, in its simplest terms, is that both useful life of a storage item and the amount of oxygen permeating a plastic film are exponential functions of temperature. By enclosing a suitable oxygen-reacting chemical system in a plastic pouch, the amount of reaction which occurs depends upon the amount of oxygen permeating the film which in turn is effectively controlled by time and temperature. In practice, the chemical system enclosed in a plastic pouch could be attached to the exterior of a storage container or placed in a special storage area where known items are stored.

B. The concept feasibility has been explored and proven through studies of the following four oxidizable chemical systems: (1). redox dye system; (2). inorganic system; (3). enzyme system; and (4). rubber sheet system.

1. The redox dye system, using an anthraquinone-zinc solution, has proven capable of conveying written messages to indicate the end of the useful life of a storage item. The written message was first covered by the blood-red color of anthrahydroquinone salt. In storage, the solution was oxidized to become colorless due to the formation of anthraquinone salt. The message suddenly becomes visible. The appearance of the message like “Discard”, or “Use Up First” is both striking and unequivocal.

2. The inorganic system, through the color change in two stages of FeCl$_2$-H$_3$PO$_4$ solution can also be used to convey information. The first stage color change, from white to greenish-yellow could be used as a warning signal that the storage product should be used up as soon as possible. When the color change arrives at the second stage, from greenish-yellow to rusty-brown, the storage product has reached the end of its useful life and should be discarded. These color changes could be easily identified with the help of a reference color chart as shown in Figure 5.

3. Both anthraquinone-zinc and FeCl$_2$-H$_3$PO$_4$ systems have been shown to be stable to light and heat. Therefore, they
could be used outdoors as well as indoors. Their applications are almost unlimited.

4. The enzyme and rubber sheet systems also could be adopted for indicating time and temperature. However, their practical applications are limited to special situations. The enzyme system, in general, is best suited for indicating time and temperature for the storage of frozen or refrigerated products. The mounted rubber sheet system is best suited to stationary objects, such as inside a warehouse or in special areas of a warehouse.

C. These studies have shown that the basic design concept provides excellent versatility. The length of time for the indicator to show a change can be adjusted at will just by changing the composition, structure or thickness of the plastic material making up the pouch. Systems can be further adjusted to provide a desired time-temperature cycle by changing the amount of reducing agent used in the redox dye system or by changing the amount of buffer solution used in the enzyme system. Therefore, the incorporation of T-T indicating system into our supply line will provide a warning system and thus greatly facilitate stock rotation in warehouses and depots around the world. Net results can be the elimination of unnecessary storage wastes and the increase of product reliability in items taken from storage.

VI. ACKNOWLEDGMENT

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VII. BIBLIOGRAPHY


Figure 1. The Chemistry of Sedox System of Anthraquinone-sulfur Solution

Figure 2. Specially Compound Rubber Sheets
Figure 3. Anthraquinone-zine System Stored at Different Temperatures and for Lengths of Storage Showing the Appearance of Hidden Message
Figure 4. FeCl$_2$-H$_2$PO$_4$ System Stored at Different Temperatures and for Lengths of Storage Showing the Appearance of Rusty-Brown Color

Figure 5. A Reference Color Chart for FeCl$_2$-H$_2$PO$_4$ System
Figure 6. Sequence of Color Changes due to Different Amounts of FeCl₂·H₃PO₄ Solution in Pouch Samples Stored at Four Temperatures (212 days)