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TIME-DELAY TEMPERATURE INDICATOR

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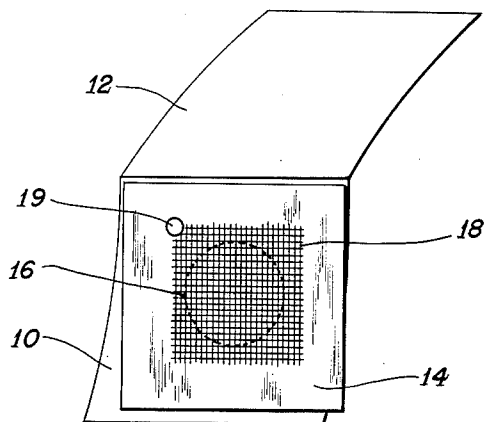


Fig. 1.

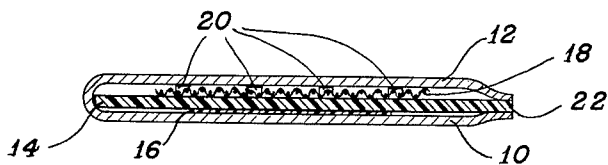


Fig. 2.

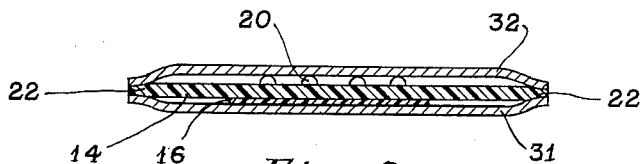


Fig. 3.

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TIME-DELAY TEMPERATURE INDICATOR

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This invention relates to temperature indicators with a built in time delay, and is particularly directed to the provision of an inexpensive indicator for frozen food packages, which will produce an irreversible indication of thawing and which can be controlled to show at any predetermined time-temperature cycle and not earlier in the cycle, which is so constructed that it utilizes a minimum of material, whereby the indicator is inexpensive enough to be economically feasible for use in individual frozen food packages, and which is small and very thin, so that it may be included in such packages without producing difficulties with handling and stacking.

The problem of determining when a frozen food package has been thawed for a sufficient time to render the contents unsuitable for refreezing is one that has plagued the industry. The time-temperature cycle necessary to really damage the food varies from product to product. Some foods can be refrozen without danger if thawed for only a short time; others can be thawed for a longer time before becoming dangerous and unpalatable. Hence, it is essential that any device used for indicating thawing be suitable for varying time-temperature cycles. For this reason, the simpler devices suggested as thaw indicators, which utilize the melting of ice for the purpose, are not satisfactory. They act too rapidly, and the time temperature cycle cannot be controlled.

More complicated devices have been suggested for the purpose of indicating thawing after a time-temperature lag. In general, because they are complicated, they are both too expensive and too bulky for the purpose. Perhaps the simplest time-lag device of the prior art is that shown in the Andersen Patent 2,560,537, assigned to the Secretary of Agriculture. This consists of a strip of filter paper in a cellophane tube, with a frozen dye solvent and a dye; on thawing, the dye solvent dissolves the dye and diffuses along the filter paper until it can be observed through a window in the package. But even this simple device is economically unsound. Because of the fact that it is necessary to color the entire strip of filter paper before the signal can be seen, the dye and solvent concentration necessary are much too large for economy. Furthermore the device is much too bulky, and not sufficiently thin to be included in small packages which must be stacked.

According to the instant invention, I provide a time-temperature controllable signal by utilizing:

(1) A spot of colorant, preferably substantially colorless colorant, capable of producing an intense color when properly treated;

(2) A reactant which has a melting point approximating the desired temperature, and is capable of producing a strong color on contact with the first material;

(3) A separating barrier which is soluble in the molten reactant over a predetermined time cycle to produce a solution, preferably a viscous solution, and which thus acts as a time-delay device; and

(4) Means associated with the reactant to prevent its spreading around the barrier when molten.

This combination ensures that all the colorant used will be viewable at the selected spot; the anti-spreading means ensures that the molten reactant will not react with the colorant until it has penetrated the barrier; and the slow solubility of the barrier in the melted reactant provides the desired time lag. Furthermore, the speed of

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penetration may be adjusted to any time temperature cycle by varying the reactant to change the speed of solution of the barrier in the melted reactant.

Thus, it is possible to get the desired intensity of color with a minimum of colorant, since all the colorant used will be visible; and thus ensure minimum cost of the colorant, which is the most expensive material in such a signal.

A typical set-up useful in frozen food packages is shown in the drawings, in which:

FIGURE 1 is a perspective view of my device, with the plies separated for clarity;

FIGURE 2 is a vertical section through the device; and

FIGURE 3 is a vertical section through a modified form of the device.

I provide a sheet of transparent material, approximately 2 x 4 inches in size and preferably made of a transparent sheeting such as cellophane, or the like, as an envelope for my device; it may be folded to form a bottom ply 10 and a top ply 12. A sheet 14 of barrier material is inserted between the folds 10 and 12. A spot of colorant 16, about 3/4 inch in diameter, is applied, preferably by printing, on the bottom ply of the envelope. A screen or grid 18 slightly larger than the spot 16 is positioned on top of the sheet 14 opposite the spot 16 by means of a drop 19 of adhesive. A few drops of liquid reactant 20 are dropped onto the screen 18, or a few crystals of frozen reactant may be used. The ply 12 is dropped into place, the edges are heat sealed 22 by fusion of the edges of the barrier material, and the envelopes are immediately dropped into storage at a temperature below the melting point of the color developing reactant.

The materials chosen for the device will vary with the use to which the device is put. Thus, while the device is most useful in the frozen food field, it could be used, by proper choice of material, for example, with certain dairy products, where the time-temperature cycle involved is concerned with temperatures substantially above the freezing point, or it would be used at ordinary ambient temperatures, as with bread, to show time elapsed since packaging.

Most preferably, I employ as the colorant material a substantially colorless base of a basic dye. Rhodamine 6 G extra base, for instance, is very light in color, and produces a very strong red coloration when reacted with an acid. Other basic dye bases may be used, with some sacrifice of initial very low coloration.

These colorants are applied as solutions in solvents which do not produce a color with them—e.g., trichloroethylene. In order to hold them in place, some binder should also be dissolved in the trichloroethylene. A satisfactory transparent binder is Arochlor 5460 (highly chlorinated diphenyl).

Satisfactory reactants for these colorants, which can be used for frozen food packs, include a number of the unsaturated fatty acids—e.g.: linoleic acid with a melting point of about 0° C., oleic acid with approximately the same melting point, and ricinoleic acid with a melting point of 0° C.—2° C. Mixtures of oleic acid and ricinoleic are especially useful. Thus, U.S.P. oleic acid alone will penetrate a .0015 inch thick barrier made from the high polymer obtained by copolymerizing 50% of styrene and 50% of isobutylene, in accordance with Smyers U.S.P. 2,274,749, March 31, 1942, in about one hour at 70° F. If 10% of ricinoleic acid is mixed with 90% oleic acid, the penetration takes three to four hours. At 15% ricinoleic acid, the penetration takes about 8 hours; with pure ricinoleic acid, penetration requires about a week. Thus, the speed of penetration can easily be controlled merely by changing the ratio of ricinoleic and oleic acid. For higher temperature reactions, the satu-

rated fatty acids can be used alone, or in admixture with unsaturated acids. In addition, I make use of hydrocarbons (e.g., n-tetradecane—melting point 0° C.) as diluents for the fatty acids and fatty oils.

For the time-delay barrier material with these reactants, I preferably employ the water clear oil soluble films made from high polymers obtained by copolymerizing isobutylene and styrene, as described in Smyers U.S.P. 2,274,749 of March 3, 1942. The solubility of these films, and the viscosity of their solutions in the fatty acids, is a function of both molecular weight of the polymer and the ratios of the monomers employed. Other film materials can, of course, be used, depending on the nature of the reactant; it is only essential that slow controlled solubility be obtained. With fatty acids, for example, I may also use polyisobutylene or polystyrene.

For the grid which prevents the spread of the molten reactant, I find textile netting to be very useful—e.g., cotton, rayon or linen netting. Glass fiber netting—18 to 25 mesh—is particularly useful. Alternately, the barrier film can be embossed in a grid or waffle pattern, so that the grid structure of the barrier acts to prevent the spread of the molten reactant.

In the modified form of the device shown in FIGURE 3, the grid structure can be dispensed with. In this form of the device, I use a separate bottom sheet of cellophane or other foil 31, on which is printed the colorant spot 16. The barrier layer 14, of exactly the same size, is positioned over the foil 31. One or more crystals 20 of frozen reactant are placed on the barrier 22, and a second sheet of foil 32 is placed over the barrier in register with the barrier and bottom sheet of foil. The assemblage is then heat sealed all about the edges to provide a heat seal 22 which now prevents the reactant 20 after melting from going around the barrier instead of through it. The heat seal 22 in this case must obviously be completed to the top foil 32 about the perimeter of the barrier.

With these same barrier materials, I can replace the dye base with any oil soluble dye, and use any oil or fat of the proper melting point to serve as a solvent for the dye to develop its color. This is not quite as satisfactory from the point of view of initial appearance, since most oil soluble dyes are colored even in the undissolved state; but the technique produces a very unmistakable signal. For instance, Sudan IV oil red, Sudan brown BB, and Sudan green BB are satisfactory colors of this sort; while peanut oil, cottonseed oil and lard oil all melt at approximately 0° C., and are good color developers. Any other combination of colorant, frozen reactant and film can be used, provided the film is soluble in the molten reactant, at a sufficiently slow rate to yield the desired penetration time. While this is easy to do for short periods of time, such combinations which yield reaction times of the order of eight hours or more, are not common.

The dimensions of an envelope in accordance with my invention can be very small indeed. The total package of the precise embodiment shown is of the order of 2 inches square; it consists of four layers of thin material in contact with each other, so that the entire assemblage is less than 0.01 inch thick. If desired, the envelope can be of other shape—e.g., round or oblong—and it can be as small as desired consonant with producing a viewable signal. This thinness and small size permit them to be inserted directly into a frozen food package or affixed to the outside by adhesive with no substantial increase of thickness, or loss of flatness in packages which must be stacked. They can be easily attached to containers of food such as milk, cream, orange juice, ice cream and meat, to pharmaceutical preparations such as vaccines and sera, or to blood plasma to record undesirable exposure to critically high temperatures for longer than a predetermined time. They can also be used to give a time-temperature

indication of staleness in items such as bread; in such cases, a reactant which acts very slowly on the barrier is desirable.

Obviously, I can use other color reactants, other films, and other grid materials than those shown to produce the desired results without departing from the scope of the invention as defined in the claims.

I claim:

1. A time-delay temperature indicator comprising a flat envelope carrying on its inside a thin barrier film of a fat soluble high polymer obtained by copolymerizing isobutylene and styrene, a spot of a basic dye base of relatively low coloration capable of producing intense color in the presence of a fatty acid, spread in a thin film, and in contact with the barrier material, a fatty reactant consisting of a long chain fatty acid with a melting point approximating the temperature desired to be indicated, which reactant when molten is a solvent for the barrier material over a predetermined time cycle and will produce an intense color on contact with the colorant, the reactant being spread in a thin layer opposite the colorant but above and in contact with the barrier film, and means associated with the reactant and lying in a plane adjacent the plane of said barrier film to prevent it spreading around the barrier film when the reactant is molten.

2. The device of claim 1, in which the reactant is a mixture of oleic acid and ricinoleic acid, and the barrier film is a fat soluble high polymer obtained by copolymerizing 50% isobutylene and 50% styrene.

3. A time-delay temperature indicator comprising a flat envelope carrying on its inside a thin film of a polymeric barrier material soluble in the fatty reactant defined below, a spot of colorant material of relatively low coloration capable of producing an intense color in the presence of said fatty reactant, spread in a thin film, and in contact with the barrier material, a fatty reactant selected from the group consisting of long chain fatty acids and oils with a melting point approximating the temperature desired to be indicated, which reactant when molten is a solvent for the barrier material over a predetermined time cycle and will produce an intense color on contact with the colorant, the reactant being spread in a thin layer opposite the colorant but above and in contact with the barrier film, and means associated with the reactant and lying in a plane adjacent the plane of said barrier film to prevent its spreading around the barrier film when the reactant is molten, said means comprising a grid on which the reactant is held.

4. A time-delay temperature indicator comprising a flat envelope carrying on its inside a thin barrier film of a fat soluble high polymer selected from the group consisting of polyisobutylene and polystyrene, a spot of a basic dye base of relatively low coloration capable of producing intense color in the presence of a fatty acid, spread in a thin film, and in contact with the barrier material, a fatty reactant consisting of a long chain fatty acid with a melting point approximating the temperature desired to be indicated, which reactant when molten is a solvent for the barrier material over a predetermined time cycle and will produce an intense color on contact with the colorant, the reactant being spread in a thin layer opposite the colorant but above and in contact with the barrier film, and means associated with the reactant and lying in a plane adjacent the plane of said barrier film to prevent its spreading around the barrier film when the reactant is molten.

References Cited in the file of this patent

UNITED STATES PATENTS

2,379,459	Schreiber et al. _____	July 3, 1945
2,823,131	Power _____	Feb. 11, 1958
2,850,393	Romito _____	Sept. 2, 1958