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Durability of a reference material over diverse conditions

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Abstract

A polyethylene film with phenolic antioxidant and phosphite synergist, has been proposed to be a standard reference material for the oxidative induction time measurement by DSC (differential scanning calorimetry) [R.L. Blaine, A proposed reference material for oxidative induction time by differential scanning calorimetry, in: A.T. Riga, G.H. Patterson (Eds.), ASTM Special Technical Publications, STP 1326, ASTM, W. Conshohocken, PA, 1997, pp. 193–204.], ASTM D-3895 [ASTM D-3895-92, Test Method for Oxidative Induction Time of Polyolefins by Differential Scanning Calorimetry]. We have examined the oxidative stability of this material over diverse conditions. These include oxidative induction time in air, over broad temperatures; induction time in pressurized oxygen in a pressure DSC, circulating oven, and samples subjected to different doses of ionizing radiation. It appears that when the lifetime is presented in the Arrhenius form, a progressively diminishing activation energies toward room temperature was observed. After combining experimental OIT (oxidative induction time) data of up to about 8 years, a conservative estimate of durability of about 30 years was obtained.

Keywords: Oxidative induction time; Differential scanning calorimetry; Polyethylene film

1. Introduction

A medium density polyethylene with peak melting point of about 125°C and about 61% crystallinity has been proposed as a reference material for the oxidative induction time (OIT) by differential scanning calorimetry (DSC). The material was stabilized by a high molecular weight hindered phenol antioxidant tetrakis- [methylene 3-(3′,5′-di-t-butyl-4′hydroxyphenyl) propionate] methane, designated as AO-1 (Fig. 1) and a phosphite synergist. Although Blaine [1] has characterized the material over several years with a multitude of standard methods, their aim was primarily to establish homogeneity and lab to lab reproducibility. Due to the widespread use of very similar materials in medical packaging, where long term shelf life storage integrity needs to be assured, and the values in understanding fundamental polymer stability, we have undertaken a study of the material over very diverse conditions, going far beyond the experimental parameters of the original reference [1].

2. Experimental

Sample for this study in the from of 220 μm (9 mil) films was kindly provided by R.L. Blaine of TA Instruments who has characterized it extensively.

ASTM Procedure D-3895 [2] is followed in the main, except air is used instead of the pure oxygen, and both the isothermal OIT and temperature scanning

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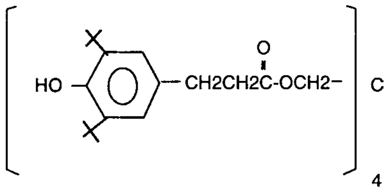

Fig. 1. AO-1 structure.

induction temperature were used. In addition, long term, oven aging studies were carried out in forced air circulating convection ovens at different temperatures with the oven aging time defined by visually detectable degraded zones typically near the film's free edges.

The oxidative induction test was conducted on a Dupont 1090 thermal analyzer with 910 DSC cell. Normally this test has two modes of measurement, that is, oxidative induction temperature and oxidative induction time. Oxidative induction temperature measures the onset of auto-oxidative reaction while the temperature is scanned at a preset rate. For this mode of testing, usually a thin and flat specimen was prepared and placed in an open aluminum sample pan secured on the thermoelectric disk of the DSC cell. The sample was then scanned at a rate of 20°C/min from ambient to 300°C or higher in an air-purging stream of 100 ml/min. The second method, the oxidative induction time, is a relative measure of the degree or level of stabilization of the material tested. The specimen preparation is the same as in the continuous temperature scanning method, except for scanning in a nitrogen gas environment to the preset isothermal testing temperature. Once temperature equilibrium has been established, the controller automatically switches purge gas to air or oxygen at the same purging rate. The changeover point to air or oxygen purge is taken as the zero time of the experiment. The oxidative induction stability of tested samples is assessed by monitoring an abrupt exotherm or endotherm departure from the baseline as indicated by Fig. 2[1].

Often, if the reaction follows a simple zero order kinetics, induction time measured at various temperatures can be used to construct an Arrhenius plot, expressed as log(OIT^{-1}) versus T^{-1}, to obtain information on the oxidation reaction kinetics. Mathematically, the rate constant K, which is proportional to OIT^{-1}, may be expressed in the Arrhenius form as:

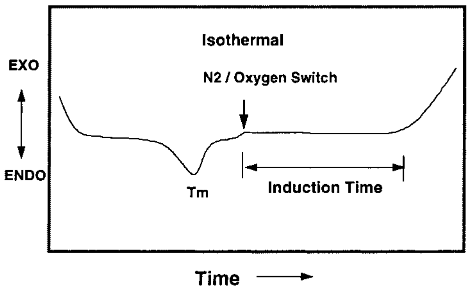

Fig. 2. OIT tracing from differential scanning calorimeter.

$$K = K_0\mathrm{e}\left(\frac{-\Delta E}{RT}\right) \tag{1}$$

Where K_0 is the pre-exponential factor, ΔE the activation energy of the reaction, R is the gas constant, and T is the absolute temperature in degrees Kelvin. The slope of the log K versus T^{-1} plot is then the activation energy divided by R.

For testing at elevated pressures, a TA Instruments pressure DSC cell (Model HP910) was used on a TA 910 cell base interfaced with a Instruments Specialist temperature controller based on a personal computer. Standard oxygen pressure of 4.14 MPa (600 psi) was used throughout the study. The cell was first pressurized to the designed pressure at a lower temperature and scanned rapidly to the set temperature. Time zero for the OIT was taken from the time the DSC cell achieves isothermal equilibrium at the set temperature.

To study the sample's durability under depleted antioxidant conditions, and/or increased peroxy free radical or hydroperoxide contents, we subjected the sample films to different levels of gamma radiation dose, carried out at a commercial medical irradiation facility at total doses of 30.6, 57.3, and 86.4 KGy at dose rates approximately about 15 KGy h^{-1}.

3. Results and discussion

Since the flowing gas medium of air instead of oxygen was used in this study, it is necessary to compare results with that of Reference [1]. Imme-

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[1] Trade Mark, Ciba Geigy.

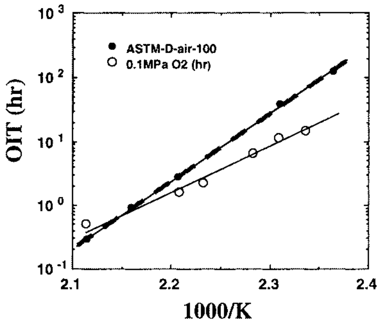

Fig. 3. Oxygen air comparison.

diately, notable difference is seen. When plotted against the reciprocal of absolute temperature, in the Arrhenius form, the data generated in air appeared to have a significantly steeper slope, or higher activation energy than that of the oxygen (Fig. 3). An activation energy of about 210 KJ/mole was measured for air, while only about 130 KJ/mole was evident for oxygen. A replotting of data at 170°C from Reference [1] at different oxygen pressures in the kinetics form of 1/OIT versus $P^{(1/2)}$ resulted in a straight line through the origin, indicating normal pressure dependence (Fig. 4). In a different medium density polyethylene system, Tikuisis et al. [3] obtained a best fit parameter of 125 KJ/mole between 150 and 200°C and oxygen pressures between 0.7 and 5.5 MPa (100–800 psi). Therefore, it appears that for the polyethylene systems studied, a significant reduction in activation energy occurred between 0.2 bar (20 KPa) and 1 bar (0.1 MPa) oxygen partial pressures (Fig. 5).

However, when the high temperature OIT data in air from 200 to 150°C was plotted along with oven aging time of 120 and 90°C, a continuous curve (Fig. 6) was obtained. This continuity indicates that OIT data in air is a more realistic experiment simulating material's oxidative behavior at lower temperatures.

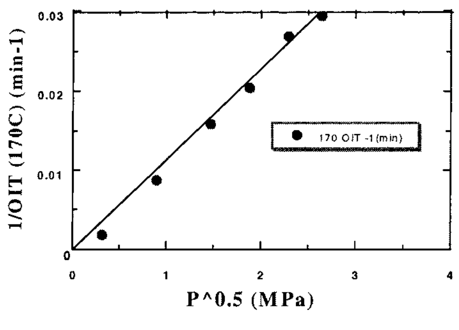

Fig. 4. Pressure dependence from Ref. [1].

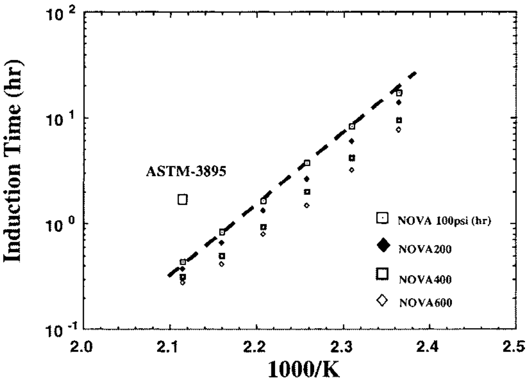

Fig. 5. Activation energy from Ref. [3].

This continuous curve behavior was very reminiscent of the data on crosslinked low density polyethylene cable compounds studied with OIT, oxygen uptake, and oven aging experiments at the former Bell Telephone Laboratories [4], (Fig. 7). When the high temperature results were extrapolated by the Arrhenius equation to lower temperatures, grossly and physically impossible optimistic results were obtained. An examination of the activation energies indicated a more than four-fold difference between the high temperatures and room temperatures (Fig. 8). This observation prompted the Bell lab researchers and others [5] cautioning against using the high temperature OIT for low temperature durability predictions. Nevertheless, by recognizing the curved nature of the durability function, one can indeed achieve more realistic predictions.

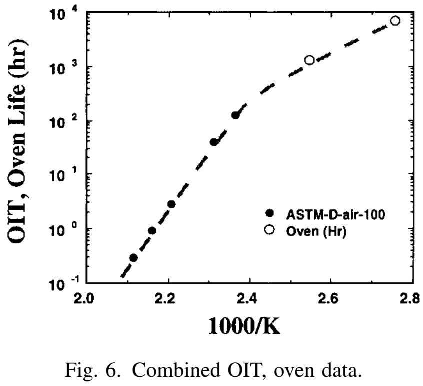

Fig. 6. Combined OIT, oven data.

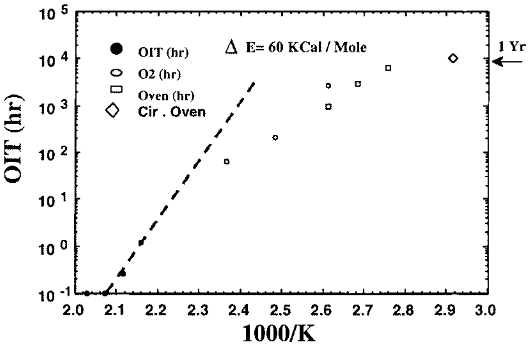

Fig. 7. Polyolefin cable OIT and oven life times.

Our own data at elevated oxygen pressures in Fig. 9 also clearly indicates that the activation energy in air, over the temperature range of 100 to 200°C, is significantly higher than that under high oxygen pressure (about 133 KJ/mole or 32 Kcal/mole). However, the high oxygen pressure data also indicates a diminishing activation energy toward low temperatures. The reduction in apparent activation energy with pressure was apparent in data in both Reference [1] and studies by Tikuisis [3]. Evidently, under high pressures, suppression of antioxidant volatilization must be responsible for at least part of the difference. However, a continuous shifting in the relative dominance of the degradation initiation versus propagation steps as outlined in Fig. 10 must also be responsible for this behavior, especially over lower temperatures.

In Fig. 11, the OIT in air data is compared with data of irradiated samples. In addition to a dose dependent drastically reduced OIT, the activation energies of these antioxidant depleted samples, although measured in air, appeared to be lower.

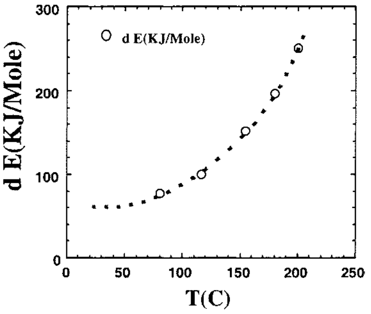

Fig. 8. Cable activation energies.

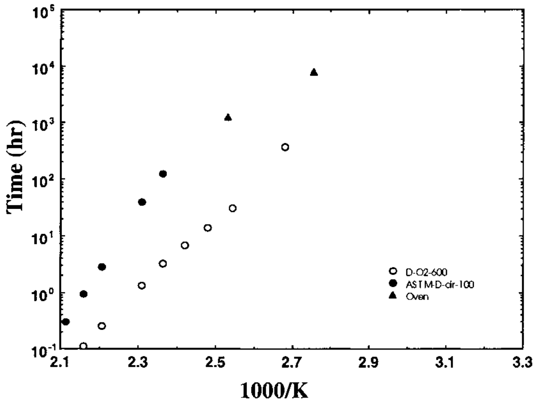

Fig. 9. Oxygen pressure vs air (4.14 MPa).

3.1. OIT behavior near phase transitions

It was observed in the sample of this study, as well as numerous other cases, when a first order transition (melting point in our case) is traversed, an one time upward shift in data. This is illustrated in Fig. 12. The shift in observed OIT correspond roughly to the effect of crystallinity. Although the direct evidence is lacking, the shift is consistent with the model that melting and crystallization effectively dilute and concentrate the antioxidant. For example, Sample D has a crystallinity of about 60%, thus upon melting, the antioxidant which typically resides in the amorphous phase would be redistributed into the entire sample, with a dilution factor of about 1/(1−0.6) or 2.5 times. This is indeed the factor observed near the melting point (Fig. 12).

3.2. Radiation effects

The near perfect coincidence of the 4.14 MPa oxygen data and the 30 KGy data in air is worth

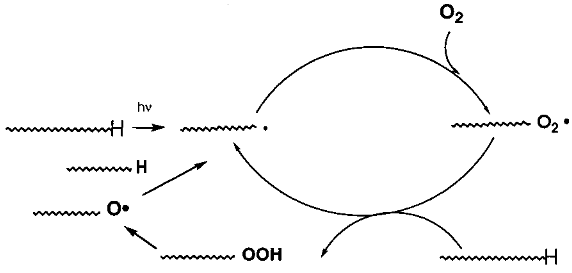

Fig. 10. Oxidative kinetic pathways.

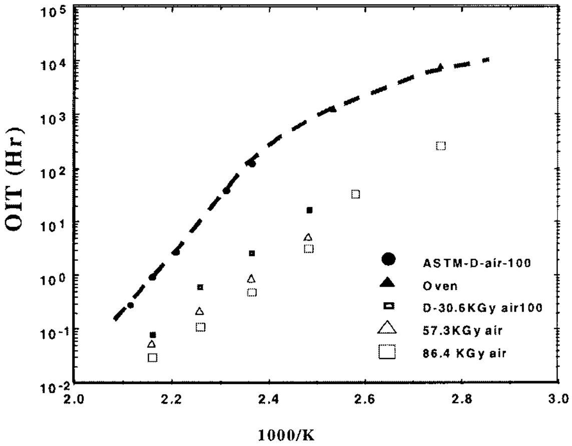

Fig. 11. Arrhenius plot of irradiated samples.

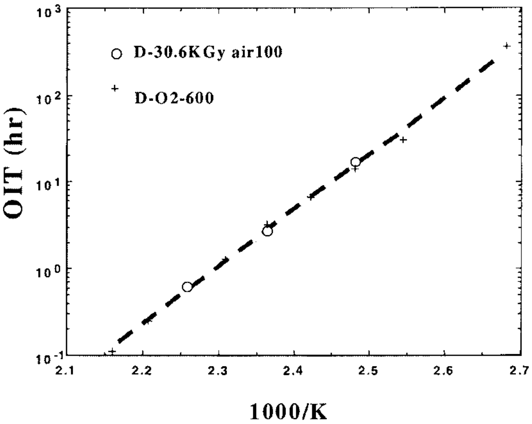

Fig. 13. Coincidence of 4.14 MPa and 30 KGy data.

commenting (Fig. 13). From our own work and others, it is well understood, that ionizing radiation severely deplete antioxidants [6], in addition, left in the polymer matrix, are significant concentrations of peroxy radicals and hydroperoxides. Both of these factors would drastically reduce the OIT. On the other hand, increasing the oxygen partial pressure would presumably increase the rate of reaction between alkyl radicals and oxygen to produce peroxy radicals. For both of the situations having the same OIT, and furthermore, the same activation energy, is indicative of substantially similar mechanisms.

To examine the activation energy among samples with different conditions, an antioxidant free, low density polyethylene film was studied. The data in Fig. 14 indicated a stability about two orders of magnitudes below that of the reference material. Nevertheless, the antioxidant free system exhibited an activation energy of about 30 Kcal/mole or 130 KJ/mole, almost identical to that of the reference material either under high oxygen pressure, or substantially depleted with antioxidants. From these, one can tentatively conclude, that the higher activation energy at atmospheric oxygen partial pressures (20 KPa) is associated with the reaction system dominated by the antioxidant, while the lower activation energy systems are dominated by the polyethylene itself. Of course, if this hypothesis can be substantiated by further experiments, it would have powerful implications on polymer stability predictions.

3.3. Ultimate durability estimates

We had earlier reported on a two segment behavior [7] (Fig. 15) of OIT in a high density polyethylene

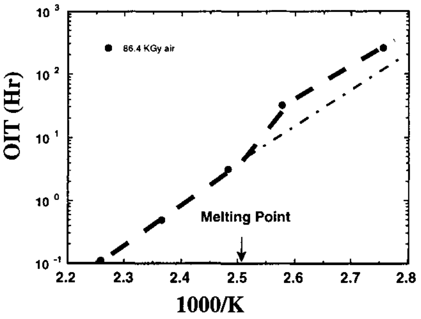

Fig. 12. OIT near melting point.

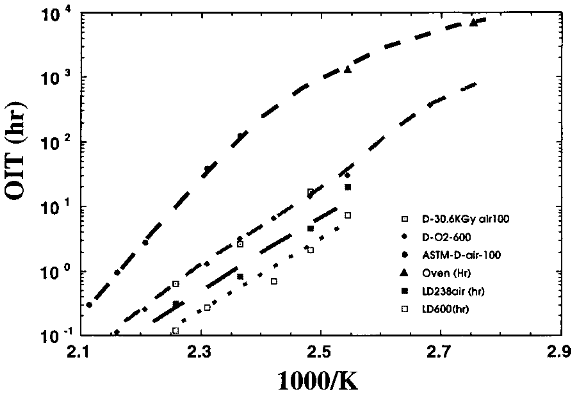

Fig. 14. Comparison with antioxidant free LDPE data.

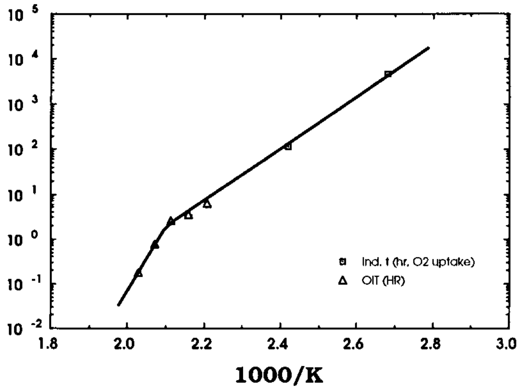

Fig. 15. HDPE OIT and oxygen uptake data from Ref. [5].

stabilized with 0.1% of AO-1. The high temperature segment was attributed to antioxidant volatilization, while the low temperature segment extrapolated to coincide with long term oven stability studies in the literature. With the understanding gained in the interim, a more refined model appeared to be more appropriate, where a continuous curvature covered the entire temperature ranges.

Since OIT is a kinetic parameter, and the proposed reference material constantly degrades with time, it is difficult to state with high certainty the ultimate lifetime under room temperature storage. Fortunately, through several runs of inter-laboratory testing, highly accurate data over several years are already available. From the OIT reduction with time, one can obtain an estimate of the ultimate durability. The central issue of how over long times, OIT's functional dependence with time, needs to be determined. In Fig. 16, the reduction in OIT at three temperatures were plotted as a function of oven storage time. It is seen that in both the 90 and 70°C cases, a two step reduction took place, and the relative height of the slow segment corresponded qualitatively to the unmelted crystalline fraction at the oven temperature. In a parallel study in our laboratories, was a high density polyethylene (HDPE) film with 0.1% of AO-1, the same antioxidant as in the reference. The 100 μm film was subjected to oven aging at 120°C and its OIT in air monitored. Fig. 17 depicts the OIT dependence with time. It is seen, that initially, a linear reduction was extended to about 10% of the original OIT before a much slower segment set in, eventually extending the ultimate life span to about three times the extrapolation intercept to the X-axis. An attractive conjecture explaining this is that the first segment deals with oxidative reactions and consumption of antioxidants in the amorphous phase where the oxygen diffusion rate and concentration of antioxidants are both high, while the second segment is the slow migration of the 'trapped' antioxidants from the crystalline domains toward the amorphous interface

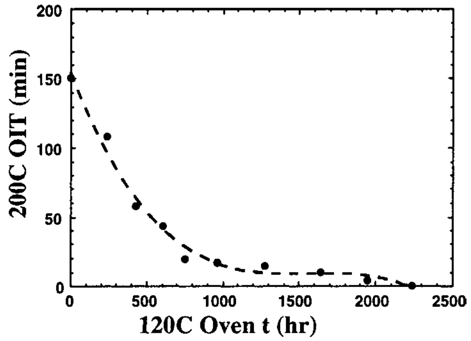

Fig. 17. HDPE OIT with oven time.

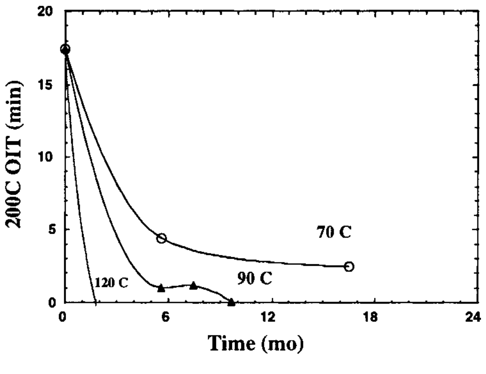

Fig. 16. Sample-D oven testing.

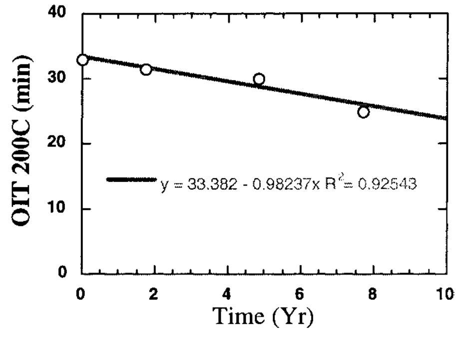

Fig. 18. OIT reduction with ambient storage.

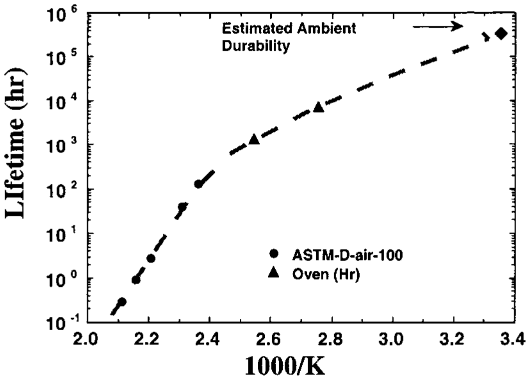

Fig. 19. Durability of Sample D.

where reaction with oxygen takes place. Nevertheless, regardless of the actual mechanism, ample experimental evidence indicated that the linear extrapolation provides a conservative lower bound for the durability.

From the data in Reference [1], a linear extrapolation indicated a zero OIT time at room temperature storage of about 33 years (Fig. 18). Of course, as time goes on, more recent data should be incorporated into the original data set to provide more accurate estimates. When the 33 year lifetime is added to the Arrhenius plot of OIT and oven lifetimes, Fig. 19 exhibited a continuous curvature with diminishing activation energies near room temperature conditions.

4. Summary

Extensive data on the proposed ASTM OIT reference material, the MDPE film designated as Sample D was gathered under diverse conditions. At temperatures above the melting point, OIT in air appeared to better correspond to oven aging data, and exhibited higher activation energies than in oxygen. Lower activation energies were also observed for antioxidant depleted samples and under elevated oxygen pressures. Upon going through the melting point, the OIT underwent a step change correlated roughly to the effect of crystallization on the antioxidant concentration. Finally, extrapolating nearly 8 years of available room temperature OIT data yielded a conservative shelf-life estimate of slightly over 30 years.

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