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Isotherms and Package Life: Some Advances in Emballistics

C. R. Oswin

11 Minterne Road, Christchurch, Dorset BH23 3LD, Great Britain

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ABSTRACT

Package-life calculations are the first evidence of 'reasonable care' in the packaging of hygroscopic goods. Three generations of emballistic calculation are traced here, from log tables via hand-held calculators to personal microcomputers. The third stage is shown to be capable of dealing with foods having isotherms that were previously intractable. In particular, packs of sugar-rich foods that switch from one isotherm to another by recrystallisation can now be provided with life-curves; they show that calculations based on the earlier formulae might result in over-protecting by a factor of two.

INTRODUCTION

The prospect (Labuza, 1982) that the Food and Drug Administration may eventually be persuaded to accept theory-based package testing as evidence of 'reasonable care' in packaging consumer goods points to the need to organise such tests on a regular basis. This paper describes a start.

Many goods deteriorate upon exposure to the environment: the spoilage is frequently caused by the oxygen or water vapour in the air. Oxygen is present in almost constant proportions, and its effect is predictable if due allowance is made for the effect of temperature on reaction rate. Water vapour is quite variable in proportion, and its effect much more sensitive to temperature change.

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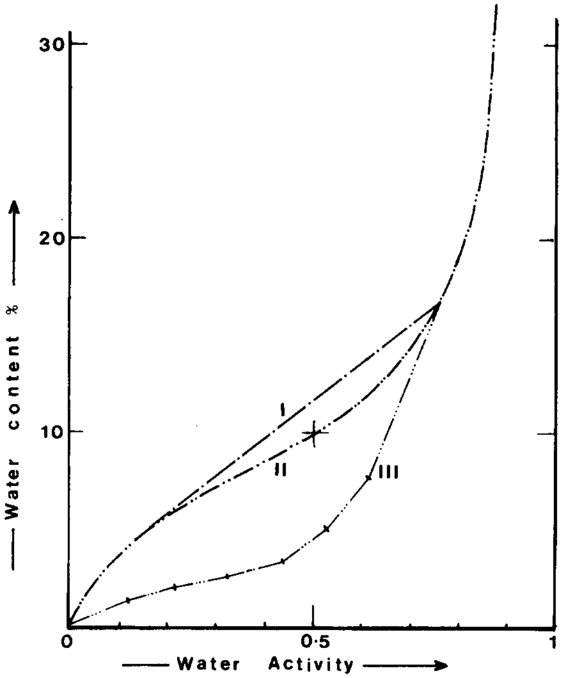

Fig. 1. Three models of an isotherm.

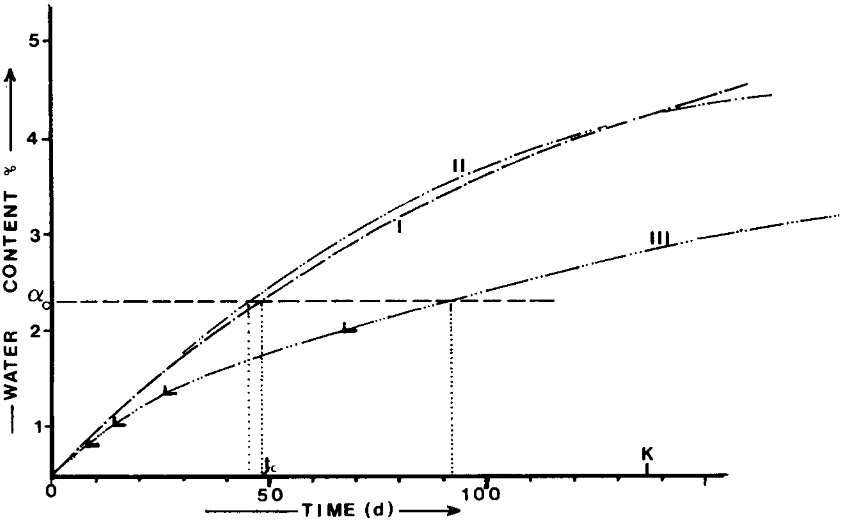

Fig. 2. Three versions of the package life curve. Accelerated test conditions.

EMBALLISTICS I

The process of packaging provides a barrier to the transfer of water between the goods and the air, but the barrier is seldom perfect. The permeability of the barrier material must be allowed for in any estimate of package life. (Package life is reckoned to terminate when the contents spoil.)

In the early 1940s some crude estimates were published (Halladay, 1942; Oswin, 1943) but they were piecemeal. Then in 1945 three independent publications (Anon., 1945; Oswin, 1945; Sharman, 1945) showed the analogy between the spoilage rate and that of a monomolecular reaction. A simple exponential equation was developed, although in line with the contemporary practice it was characterised by the half-life of radioactivity rather than by the time-constant of a physical relaxation process. The use of log tables to calculate the life curve was tedious and the simplifying assumption that the isotherm of the hygroscopic food, relating the equilibrium moisture content to the relative humidity of the storage atmosphere, was a straight line, was not accurate. However, it was accepted in view of the usual uncertainty of storage conditions in practice. The equation was subsequently validated by research associations (Heiss, 1948; Paine, 1951). Line I in Fig. 1 depicts such a linearised isotherm, and line I in Fig. 2 is the corresponding life curve. Line I in Fig. 2 cuts the ordinate of the critical water content (α_c) at an abscissa corresponding to a critical time (t_c). This is the predicted shelf life—here about 50 days.

EMBALLISTICS II

In 1946, a survey of the equations proposed for isotherms showed that in general the best fit was given empirically by one of Pearson's frequency curves (Oswin, 1946). The choice was subsequently confirmed (Labuza *et al.*, 1972; Boquet *et al.*, 1978), but it led to no immediate progress because no standard integral was available. Only in 1972, with the advent of cheap personal calculators, was it noticed that a simple bionomial equation gave a close approximation to the expanded integral, and that the 'Sinclair Cambridge' had a peculiarly suitable facility for this (Oswin, 1975). Line II in Fig. 1 is this binomial isotherm, and line II in Fig. 2 is the life curve obtained.

The Pearson equation was selected on an empirical basis, but it has since been derived, by an approximation, from the standard BET isotherm (Caurie, 1981). It had previously been used only in the simplest form with $m = 2$ (Trouton & Poole, 1906; Kaneko & Ikenaga, 1941).

EMBALLISTICS III

The binomial equation gave a fair fit with many goods, but like the previous one (Grover, 1947) it was unsatisfactory for foods that contained a high proportion of sugar. The isotherms of such foods had a flatter section in the middle, and then rose sharply at higher humidities as the sugar began to deliquesce. The situation is even more complicated if the sugar is present as a dried syrup or juice, because it is then in the hydrated, amorphous form: virtually a supersaturated solution. When it crystallises, water is released.

COMPOSITE ISOTHERMS

The isotherm for amorphous sugar is usually shown (Bushill *et al.*, 1965; Karel, 1975) with a steep drop at about 0·4 water activity, because that is what is observed when the food is exposed in an atmosphere of constant humidity. Water is released and escapes into the air. This cannot happen inside a small pack without altering the humidity of the contained microclimate: so the water is reabsorbed into the food and the water activity rises rapidly. In a good pack it can be assumed that release and reabsorption are concurrent. This is shown in line III of Fig. 1, with a corresponding life curve in line III of Fig. 2. The transitions are shown in more detail in Fig. 3: the dehyrated food starts on a desorption isotherm. The first change is across a 'tread' to an adsorption 'riser'. Then at about 0·4 water activity the sugar crystallises and there is a transition to the anhydrous-adsorption curve, which is followed in the final stage.

MICROCOMPUTERS

Such a complicated isotherm would be tedious to use in calculating life curves. Computer solutions have been proposed for non-linear isotherms

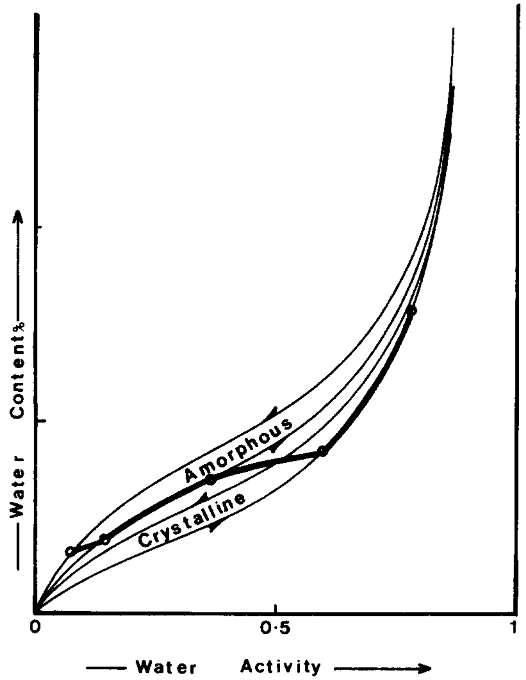

Fig. 3. Transition from one set of isotherms to another.

(Peppas & Khanna, 1980) but the advent of cheap personal microcomputers has changed the situation radically. The isotherm can be taken as a series of straight lines, and exponential integrations performed sequentially. This is well within the capability of a Sinclair ZX81 (16K). (It would be easy to use a standard program to fit an *n*th-order polynomial by regression, and to integrate that: but trials showed that the fit was not very good near the 'corners'. Attempts to improve this by going to higher orders merely generated unwieldly values for the higher coefficients.) When such a program is set up, the older emballistic equations become superfluous. The only loss is that an isotherm can no longer be characterised by two parameters. The benefit of the computer is seen in line III of Fig. 2, where the product (time × permeability) is twice that required by curves I and II. Dividing this product by the shelf life required for a particular market gives the maximum allowable permeability. Some degree of overprotection is, of course, desirable (Oswin, 1943; Labuza, 1982), but it should be calculated rather than haphazard or cumulative.

UNITS

There has been no advance in the units used for emballistic calculation: SI units are not convenient, because reckoning in 'mole water per Newton-second' gives the shelf life in seconds while the market requires it in months. There are few permeability units that include the essential factor of water vapour pressure gradient, so the pre-War units of Carson (1937) have been revived and permeabilities converted to grams water per square metre per day per millimetre of mercury. One Carson unit is approximately equal to 5 picomole per Newton-second.

Water activity is used in preference to Equilibrium Relative Humidity following the practice of Gane (1943).

ACCELERATED TESTING

It is always desirable to be able to speed up tests which refer to long package life. This is usually done by raising the storage temperature, but the results are not entirely trustworthy because temperature affects so many factors. The permeability is increased exponentially (Oswin, 1945) but the isotherm is also modified. It is easier to use 'pilot' packs made from a material of higher permeability and of identical size. The results can be plotted for both packs if (time × permeability) is used instead of time as the independent variable, rewriting the usual equation

$$t = \frac{W \times \mu}{P \times A \times p} \ln \frac{(\alpha_s - \alpha_0)}{(\alpha_s - \alpha_t)}$$

in the form

$$P \times t = \frac{W \times \mu}{A \times p} \ln \frac{(\alpha_s - \alpha_0)}{(\alpha_s - \alpha_t)}$$

where t is the time elapsed, W the (dry) weight of goods, μ the slope of the linear isotherm, A the area of wrapping, P its permeability, p the saturated water vapour pressure in mm Hg, and α the water content of the contents (on a moisture-free basis) at times 0 (initial), t and s (equilibrium). In SI units (time × permeability) would be the quantity mole per Newton.

PILOT GRAPHS

The multiple plot in Fig. 4 shows the diagnostic and prognostic values of the pilot pack. The points A–A–A–A indicate a high-permeability pack: useless in the market but valuable in the laboratory for confirming the prediction: B–B–B–B is the good market pack, responding too slowly to discriminate between the curves. Errors in the data (poor seals, damage or screening) would show as C–C–C–C or D–D–D–D. When a curve is established by the pilot, it is only necessary to read off the value of (time × permeability) corresponding to the maximum water content that can be tolerated without spoilage and to divide it by the intended "best used by..." life to give a specification for permeability in the wrap.

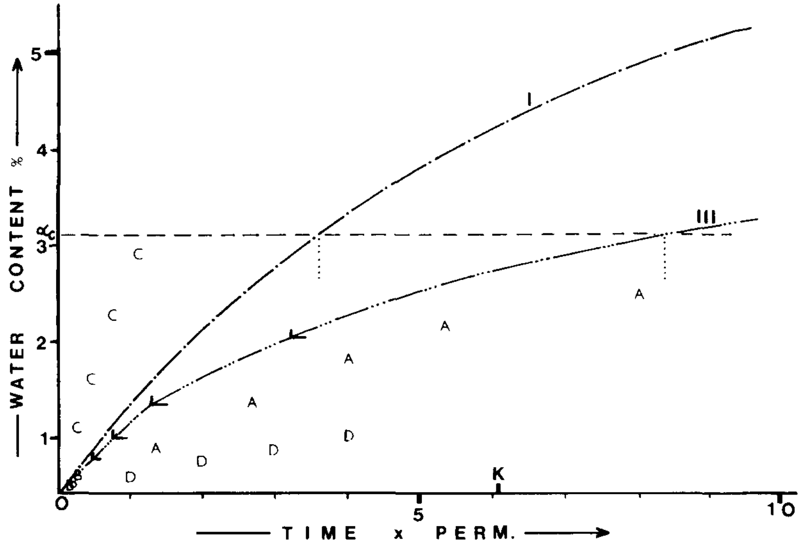

Fig. 4. Shelf life curves for pilot and market packs.

EXPERIMENTAL RESULTS

By courtesy of General Foods Ltd, Banbury, Oxon, UK, it is possible to quote the results of two sets of laboratory tests. One set (Table 1) shows the observed water content in packs of a dry-mix dessert powder (product X) containing hydrated, amorphous sugar. These tests were accelerated (about five-fold) in the conventional way by exposure to conditions of

TABLE 1
Product X at 85/32

Time × permeability	*Water content of the contents*		
	Calculated I	*Calculated III*	*Observed*
0	0·9	0·9	0·9
0·375	1·5	1·47	1·3
0·75	2·06	1·95	2·0
1·125	2·6	2·29	1·9
1·5	3·12	2·58	2·6
1·875	3·61	2·81	2·7
2·25	4·06	2·96	2·9
2·625	4·56	3·12	3·1
3·0	5·0	3·34	3·6
3·375	5·41	3·56	3·8
3·75	5·8	3·76	4·1
4·5	6·59	4·04	4·0

Equilibrium water content: 7·0. Critical: 2·3.

TABLE 2
Product Y at 75/24

	Time × permeability	*Water content of the contents*		
		Calculated I	*Calculated II*	*Observed*
M	0	0·45	0·45	0·45
M	0·014	0·465	0·465	0·47
M	0·028	0·48	0·48	0·47
M	0·042	0·494	0·49	0·55
M	0·056	0·51	0·51	0·47
M	0·084	0·54	0·53	0·56
M	0·098	0·55	0·54	0·55
P	1·33	1·58	1·33	0·89
P	2·66	2·56	1·87	1·38
P	4·0	3·34	2·29	1·83
P	5·33	3·95	2·61	2·17
P	8·0	4·9	3·05	2·48

Equilibrium water content: 6·5. Critical: 3·1. M = market pack. P = pilot.

85% RH and 32 °C. Similar tests conducted at 75/24 had not reached the point of divergence between the old (I) and new (III) curves by the time the tests were terminated. The value taken for the permeability was the average of a set ranging over ±18%. Water content was determined consistently by Karl Fischer analysis.

The second run (Table 2), used pilot packs (product Y) that were almost a hundred times as fast as the market packs. Each point required the ablation of a pack for organoleptic tests, so the validation is not complete, but the results are closer to the predictions of the new emballistics than the old. All the sugar in this dry-mix dessert powder was crystalline.

The ratio of the package lives at the critical water content, as predicted by the old and new methods was 7·88/3·64, or 2·16—so the old method would have resulted in unintentional overpackaging. The early results strongly indicate an induction period in the pilot packs of about 3 days. This would reduce the calculated values by 0·5, and make the fit as good as that in Table 1.

CONCLUSIONS

When a food contains a high proportion of sugar—particularly an amorphous sugar—the predictions of shelf life given by earlier emballistic calculations may be unduly pessimistic. Computer predictions using the measured points of the isotherm may make feasible a reduction in packaging specifications.

The calculations must be verified by tests. It is an advantage if non-destructive methods are used for following the change in water content.

No conditions have been specified for 'best used by...' date-marking. To remove uncertainty, the authorities should define the environment implicit in their regulations.

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