

# Moisture Permeability of Wax-containing Films

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## Introduction

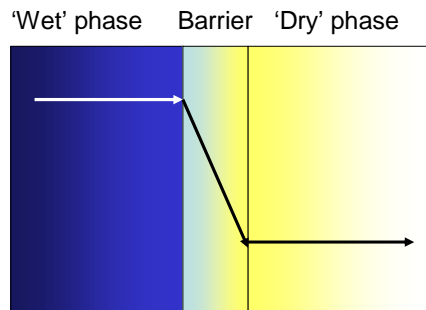
As consumers demand more and more variety and innovation in food so commercially made products incorporate a greater complexity than ever before. Multi-component and multi-textural products are now commonplace with some parts of the product being dry and crispy whilst other parts are moist and soft. At the same time as consumers are demanding these increasingly complex products they, as well as the manufacturer and the retailers, are demanding extended shelf-lives.

The two demands are often in conflict. Multi-component, multi-textural products inevitably mean that some ingredients are going to migrate into other parts of the product. It may be a movement of fat from one phase to another causing change in the hardness and softness of these phases and, possibly, bloom formation if one of the phases is chocolate. Or, it may be a movement of water from a soft moist phase into a dry crispy phase resulting in the loss of the initially multi-textural characteristics of the product.

Both of these are caused by diffusion (Figure 1), a process in which there is movement of a substance, in this case water, from a phase of higher concentration to a phase of lower concentration with, essentially, a concentration gradient within any barrier that might be present.

Figure 1

## Moisture migration as a result of diffusion



Although both fat and moisture migration are fundamentally similar processes in physical terms, I would now like to concentrate solely on the phenomenon and problem of moisture migration.

There are various ways of reducing the degree of moisture diffusion or the degree of moisture migration occurring in products. One is to reduce the 'driving force' by, for example, more closely matching water activities of the phases. Unfortunately, this often means compromising on the textural differences which means that, in many cases, the use of some form of barrier between the moist and dry phases is necessary.

If we take the general principle of 'like attracts like' then clearly to repel moisture we need to have a film based on an 'unlike' material, i.e. a hydrophobic material. Films produced from lipids have these characteristics. In this context I shall consider two main forms of lipid - triacylglycerols or triglycerides, and waxes. There is, however, also a third type of lipid which has been used in moisture barriers and that is the group of acetylated monoglycerides, essentially triglycerides containing both a long chain fatty acid and two acetic acid groups.

Both fats and waxes have a long history of use in minimising moisture movement. For example 'larding' which was a process of coating food in fat was used in 16th century England to minimise moisture loss [Labuza TP, Contreras-Medellin R - *Cereal Foods World* 1981;26:335]. Wax coatings are often used on fruit such as lemons and apples and on vegetables such as cucumbers and peppers [Guilbert S - 'Technology and Application of edible protective films' in *Food Packaging and Preservation: Theory and Practice* (M. Mathlouthi), Elsevier Applied Science, London]. Whilst such coatings help to reduce moisture loss they can also have other desirable or even undesirable side-effects. For example, too much wax as a barrier on lemons can allow fermentation of the fruit to occur [Anonymous - 'Invisible package .. long life to fruits and vegetables', *Mod. Pack.* 1944;18:75-80]; coating some vegetables can affect the rate of respiration resulting in off-flavour development.

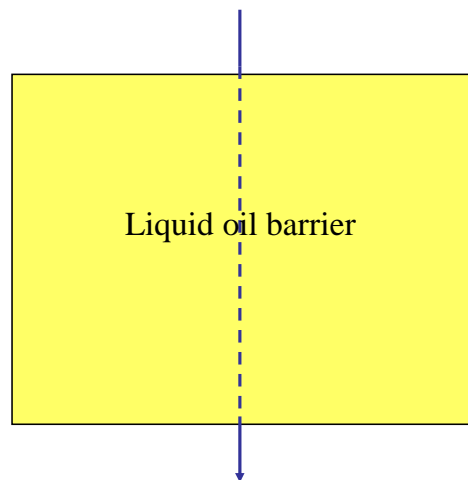
Thin wax-based coatings are often applied to nuts, raisins and some confectionery products to both give them a glaze and to stop them sticking together. Frozen meat and fish are sometimes coated in barriers to prevent oxidation, dehydration and freezer burn. And, finally, the use of wax coatings on cheeses such as Gouda, Edam etc are well-known.

In all of these cases the barrier, often a wax barrier, is used to either retain moisture within the product or to prevent some external factor from entering the product. In none of these cases, however, is the barrier used to stop the movement of, say moisture, from one part of the product to another. It is this type of barrier use that I would like to concentrate on.

### How do lipid-based moisture barriers work?

To understand how lipid-based moisture barriers work and to define the factors which are important in terms of their performance we can use simplified diagrams of a moisture barrier.

Figure 2



If we start with a simple barrier of 100% liquid oil - shown in Figure 2 with the moist phase of the product above it and the dry phase below it - then as a molecule of water meets the interface between the barrier and the moist phase it will dissolve in the liquid oil. So, water at that interface will dissolve in the liquid oil barrier until the oil becomes saturated with water. According to Bailey, the solubility of water in an oil such as winterised cottonseed oil is 0.141% at 32.2°C [Bailey's Industrial Oil and Fat products, Vol. 1, 4<sup>th</sup> edition, 1979]. Because of the low solubility of water in oil, this saturation level will be such that only a small amount of water will physically be dissolved in the barrier at any one time. However, what water is dissolved will diffuse through the barrier following the laws of diffusion until it reaches the dry phase at the other side of the barrier when it will be readily absorbed into the dry material. To maintain the saturation of water in the oil barrier, as soon as one molecule of water has diffused through the barrier and become absorbed into the dry phase another molecule enters the barrier from the moist phase. And so it goes on, with moisture

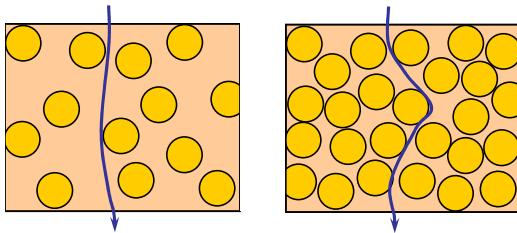
gradually being transferred from moist to dry phase through the liquid oil barrier. Although it may sound as though the barrier is therefore quite useless, this is not, in fact the case, because even a barrier of 100% liquid oil will slow down moisture migration compared to the comparable situation where no barrier is present.

To improve the barrier properties, however, we need to try to do two things. Firstly we need to increase the path length so that it takes longer for the moisture to move from one side of the barrier to the other. Secondly we need to reduce the amount of moisture physically present at any one time in the barrier layer. At first sight, these two requirements seem to be mutually exclusive. To increase the path length would seem to mean having a thicker barrier layer; having a thicker barrier layer would allow more water to be dissolved. And, anyway, increasing the barrier thickness would mean making it more obvious and hence less acceptable to the consumer.

There is, however, a very simple solution to this - increase the amount of solid fat in the barrier (Figure 3).

Figure 3

### Void Fraction or Porosity

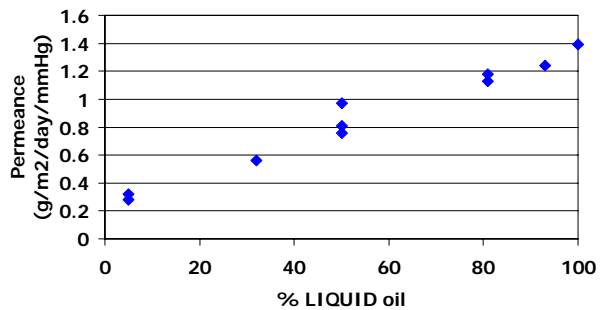


Assume that we have a barrier of about 250 microns thick. This is a common thickness for commercially used moisture barriers. Moving from a barrier containing no solid fat to one containing 50% solid fat would mean only half the amount of liquid oil is present. This means that only half the amount of water is present at any one time - but the barrier thickness is the same - 250 microns. The path length, however, has increased to considerably more than 250 microns because the water molecules now have to move farther to get to the other side of the barrier, now having to circumnavigate all the solid fat crystals. Increasing the solid fat content further to 80% means that only 20% liquid oil is present so only 20% of the original moisture content is present in the barrier layer and there are even more solid fat crystals present as obstacles to movement.

So, there is a general relationship between the liquid oil content of the barrier and its permeability (Figure 4).

Figure 4

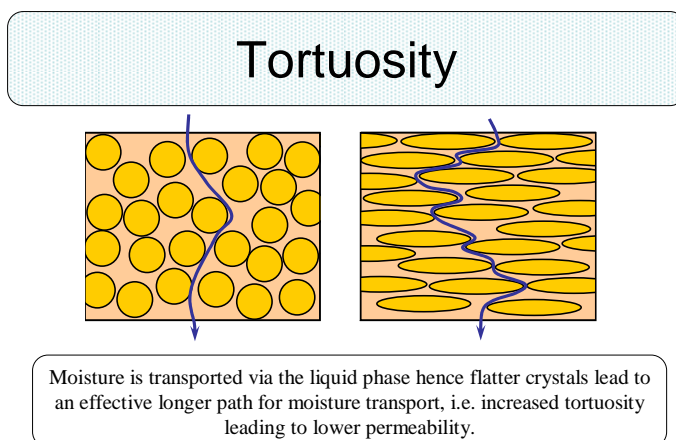
## Effect of solid fat content on permeance



There is, however, a limit to how far we can go with this before reaching a point of no further improvement. One of the reasons for this is the way in which fats generally crystallise. A barrier based on a partially hydrogenated vegetable fat, for example, will crystallise in a spherical form known as spherulites.

If, instead of crystallising in this form we could force it to crystallise in flat plate-like crystals then we could increase the path length of moisture movement further by increasing the tortuosity of the barrier system (Figure 5). This is where the waxes in the barrier can help.

Figure 5



The polymorphic form of the fat barrier can also have an influence, although there are conflicting results here. Kester and Fennema [JAOCS 1989;66:1147-1153] found that the alpha form of a barrier of fully hydrogenated soyabean and rapeseed oil had a lower permeability than did the beta-prime form even though the beta-prime form would have had a denser crystal structure. Work carried out in our own laboratory, however, on tempered and untempered cocoa butter showed that the untempered form had a permeability about 13 times greater than did the tempered form.

### Measurement of Permeability

Permeability is normally expressed either in

$$\text{g.mm/m}^2.\text{d.kPa}$$

or in

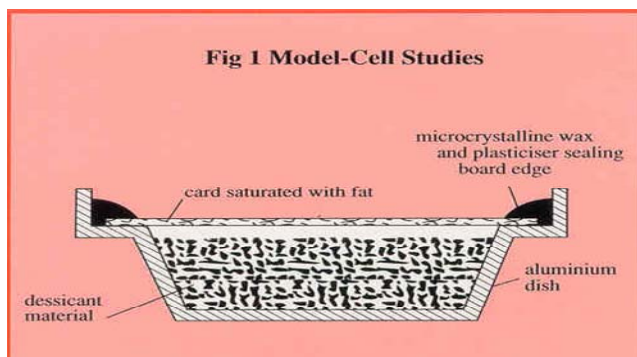
$$\text{g.mil/ m}^2.\text{d.mmHg} \quad \text{where 1 mil is one thousandth of an inch}$$

In our own work reported here we use the second set of units. To convert these units into the first set of units simply multiply by 0.19.

There are three main ways to measure permeability - (a) a manual dry-cup method, (b) a manual wet-cup method, (c) instrumentally using a water vapour transmission rate (WVTR) measurement.

Figure 6

### Dry-cup method

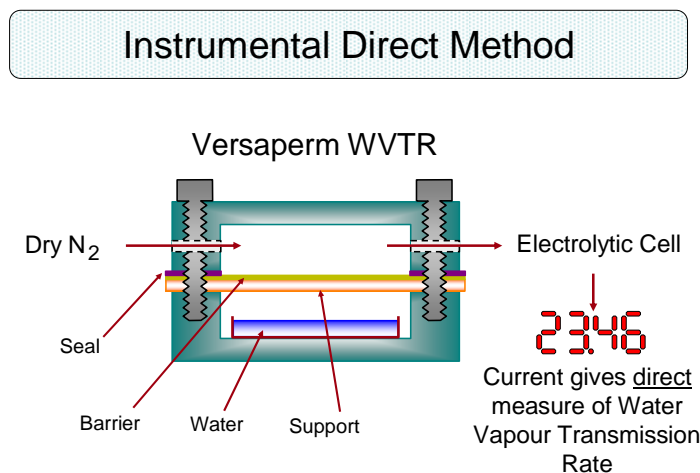


In the dry-cup method (Figure 6) the test sample is sealed to the open mouth of a test dish containing a desiccant and the whole is placed in a controlled atmosphere. Periodic weighing determines the rate of water vapour movement through the sample into the desiccant. In the wet-cup method the dish contains distilled water - again weighing determines the rate of water movement into a controlled atmosphere.

Clearly the dry-cup method involves water gain whilst the wet cup method involves water loss.

Both of these methods are time-consuming and so we have generally used the third method - digital WVTR measurement (Figure 7). The principle is very similar to the wet-cup method. A dish of water or saturated salt solution is placed in a cell above which the sample is sealed. Dry nitrogen is passed across the top of the sample and an electrolytic cell measures the moisture present in the exiting gas. Using a fixed sample area and a known flow rate for the gas allows the instrument to calculate the WVTR in  $\text{g}/\text{m}^2.\text{d}$ .

Figure 7



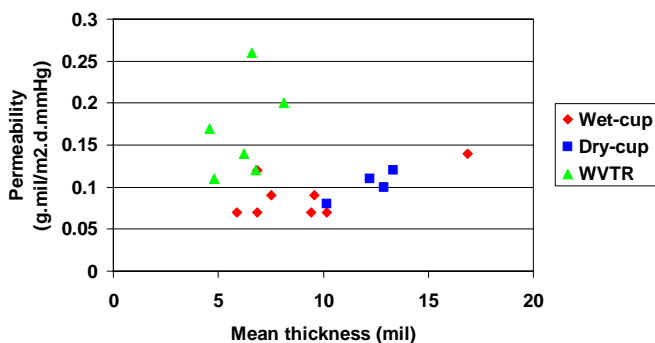
Source: K.W. Smith  
Unilever Research

Having simply a lipid film is all but impossible both because it is extremely difficult to mould, transfer and seal such a film within the apparatus without damaging it and because doing this would restrict us to fairly high solid fat content films. So, irrespective of which method is being used it is necessary to have some form of support for the lipid barrier. For this reason all of barriers we evaluated are painted as evenly as possible on Carton-Cote. Carton-Cote is a thin permeable card with a glazed face (on which the barrier is applied as evenly as possible). The thickness of the barrier is calculated by weight difference before and after application. The permeability of the card itself is so high that the instrument is unable to measure it. This means that, to all extents and purposes, the permeability which we measure is the permeability of the lipid film.

Because the thickness of the barrier layer is included as a function within the permeability units the permeability (as a number) should be independent of the barrier thickness. This tends to be more the case with the two manual methods - wet-cup and dry-cup - than with the digital WVTR method as can be seen in Figure 8. The scatter of points is much more with the WVTR method than with the two manual methods.

Figure 8

## Comparison of permeability measurement methods



Taking the mean of a number of digital WVTR replicates does, however, give us permeability measurements of a reasonable accuracy.

### Waxes in barriers

Waxes are esters of long-chain alcohols with long-chain fatty acids – long, in both cases, meaning 16 or more carbon atoms. We can give a ‘carbon number distribution’ to the waxes by adding the numbers of carbon atoms in both the fatty acid and alcohol chains. As far as use in food products is concerned we can divide waxes into three main groups depending on their source – mineral, animal and vegetable.

The main mineral wax is paraffin wax and, although it is approved for use as a food coating on, for example citrus fruits, it is not generally used within foods as a moisture barrier. Indeed, there has, over the past 10-15 years, been a strong move away from the use of mineral hydrocarbons in foods prompted both by legislative changes and consumer demands.

Of the animal-sourced waxes used as a food coating, beeswax is probably the most important. This is produced by honey bees during the construction of their honeycomb cells. It has GRAS (generally recognised as safe) clearance by the US Food and Drug Administration and can be used at levels of below 0.1% on a range of confectionery products.

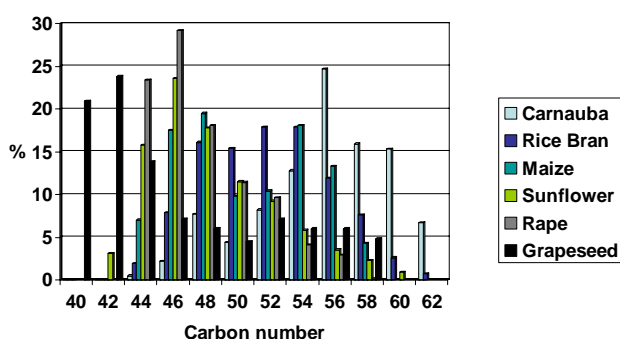
As far as food products are concerned, the use of waxes from vegetable sources is far more common with candelilla wax, carnauba wax and rice bran wax being widely used. Candelilla wax is found in the *Euphorbia* species in Texas and Mexico and although it does contain some wax esters it is mainly composed of hydrocarbons. Carnauba wax is found in the *Copernicia Cerifera* ‘Tree of Life’ in Brazil and is almost totally wax esters. Other, more common oils, such as sunflower oil, rapeseed oil, grapeseed oil and maize oil also contain some wax esters, although they are, of course, mainly composed of triglycerides. The wax content of some of these oils – sunflower oil is a

good example - is such that they need to be 'winterised' before bottling to ensure good clarity.

The carbon number distribution of the wax fractions of these oils differ considerably with carnauba wax having the longest chains and grapeseed oil wax the shortest (Figure 9). The waxes from sunflower oil and rapeseed oil are very similar in their carbon number distribution.

Figure 9

### Carbon number distribution of common vegetable waxes



Although such waxes can be used on their own as barriers within foods they are more generally used in combination with other lipids such as triglycerides and acetylated monoglycerides. Indeed, the moisture barrier developed by Danisco under the name of the Grindsted Barrier System is made up of a blend of acetoglyceride and beeswax.

### New developments from Loders Croklaan and Unilever Research

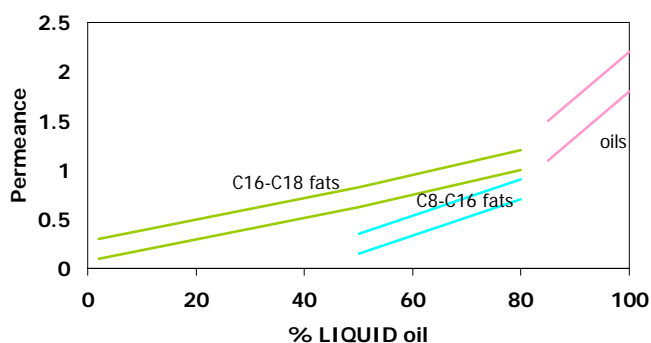
Over the past 10-20 years Loders Croklaan, working together with Unilever Research at Colworth House, has extensively studied the phenomenon of moisture migration and the use of both triglyceride-based and wax-based barriers as a means of minimising such migration.

As would be expected from the description already given of how moisture moves through a fat barrier, there is a general relationship between the permeability and the solid fat content (or, in reality, the liquid oil content) of the barrier. These early results (Figure 10) were produced using the manual dry-cup method and showed that at high liquid oil contents all oils, essentially, perform in much the same way. They also suggest that at very high solid fat contents fats also perform in much the same way, irrespective of their nature. In the centre of the diagram, at medium levels of liquid oil or solid fat there appears to be a chain-length effect in which fats with short to medium chain length fatty acids have a slightly lower permeability than longer-chain fats. In this lower-permeability group are fats based on, for example, milk fat, palm kernel oil, coconut oil. A potential problem with using these types of lauric fat

as a moisture barrier is, of course, that of hydrolysis. If hydrolysis of the fat barrier were to occur - and this is always a possibility when they are obviously adjacent to a water-containing phase - then free fatty acids will be generated. With lauric fats, only a small degree of hydrolysis is necessary to give a soapy off-taste.

Figure 10

### Moisture migration through card saturated with fat



This work progressed and resulted in the development and commercial production of two moisture barrier fats. One (barrier fat A) typically contained about 60% solid fat (or 40% liquid oil) at 20°C and had a permeability of 3.8; the other (barrier fat B) typically contained about 80% solid fat (or about 20% liquid oil) at 20°C and had a permeability of about 2. This again showed the good relationship between liquid oil content and permeability in that halving the liquid oil content halved the permeability. To go much lower, however, involved moving into a completely different area of technology and involved us in starting to look at vegetable waxes.

The literature would suggest that waxes should make good moisture barriers and there is also evidence to show that some waxes crystallise in a plate-like form which is the type of crystal form we felt was necessary to increase the tortuosity such that we could reduce permeability further. However, brittleness of such wax films is a major problem.

Table 1 Permeabilities of waxes

Wax source	Permeability (g.mil/m <sup>2</sup> .d.mmHg)
Beeswax	0.18
Paraffin wax	0.27
Candelilla wax	0.73
Carnauba wax	0.84
Rice bran wax	2.14

As a start, we measured the permeability of a number of waxes that had been used as barriers or coatings in foods (Table 1). The vegetable waxes all have a higher permeability than either paraffin wax or beeswax and also have a tendency to crack. This is clearly the explanation for the high permeability of rice bran wax.

In order to reduce this tendency to crack the waxes can be blended with other, more 'flexible' materials. One approach adopted by the Danisco company has been to blend a wax such as beeswax which has a very low permeability but poor flexibility with an acetoglyceride which has good flexibility but a much higher permeability. The approach which we took, however, was to look at blends of vegetable waxes and fats. In other words to blend waxes not with acetoglycerides but with triglycerides.

The starting point was the moisture barrier already referred to as barrier fat A which had a permeability of 3.8. Blending this with up to 10% vegetable wax resulted in different degrees of reduction of permeability (Figure 11). The best results were obtained when 5% or 10% candelilla wax was added where permeabilities of less than half of that of the original barrier fat were achieved. Rice bran wax reduces the permeability as up to 4% is added but then levels off at a permeability of about 3. Carnauba wax reduces permeability from 3.8 to about 2.8 when 5% is added. Despite seeing improvements to the permeability of the barrier these improvements were in many cases no better than those which could be achieved by simply reducing the liquid oil content of the fat barrier itself - and they were only achieved by the use of fairly specialised waxes.

Because of this we began to look at other wax sources and, particularly, the wax that can be obtained from sunflower oil.

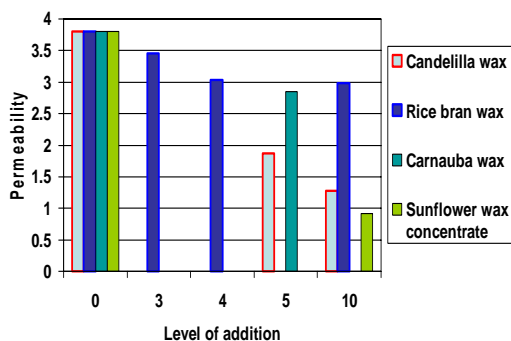
Crude sunflower oil contains between 0.02% and 0.35% wax which, at ambient temperatures will crystallise in the oil giving a cloudy product. Producers of bottled sunflower oil prefer to remove this cloudiness so that when the consumer buys the oil it is clear and bright in the bottle. The wax is therefore removed by winterisation. Winterisation is effectively a low-temperature dry fractionation process in which the wax is allowed to crystallise out and is removed by filtration. Even this wax concentrate, which I shall refer to as 'sunflower stearine' because it also contains some of the higher-melting sunflower triglycerides, contains more triglyceride than wax with wax levels varying from 1% up to 10% depending on the wax content in the starting oil and the process being used to separate the stearine. Typically, wax levels of about 6% are found.

In theory, it is possible to concentrate the wax further by a more specialised fractionation process and we were able to obtain a product containing up to 50% sunflower wax in a laboratory fractionation of the sunflower stearine. The permeability of this 50% concentrate was 0.47 which compares favourably with the permeabilities we measured on candelilla, carnauba and rice bran waxes.

When added at a level of 10% to barrier fat A a considerable reduction in permeability was observed (Figure 11).

Figure 11

## Reduction permeability by adding vegetable waxes to Barrier Fat A



Scale-up of this fractionation process was, however, very difficult in terms of obtaining a sufficient degree of concentration of the wax whilst, at the same time obtaining a commercially viable yield.

If, however, we consider the last result in which 10% of the 50% sunflower wax concentrate was added to barrier fat A we essentially have a blend of 90% vegetable fat with a solid fat content at 20°C of about 60% (barrier fat A) with 5% sunflower wax and 5% sunflower oil. The sunflower stearine (the solid fraction from the winterisation process) contained typically about 6% wax. It is clear, then, that the wax content of this stearine and the wax content of the blend of barrier fat A and 50% concentrate are very similar.

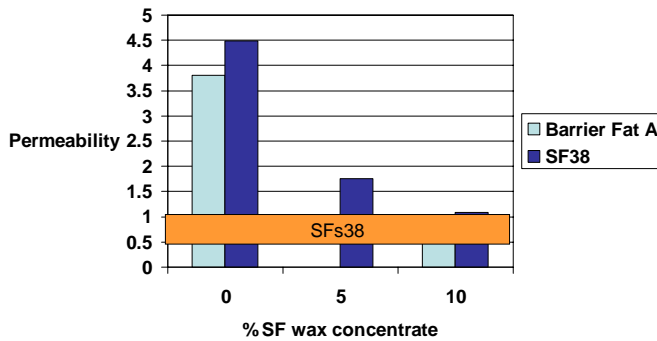
This then invited the question - instead of trying to concentrate the wax to 50% and then add this at a level of 10% to an existing barrier fat, why not simply hydrogenate the sunflower stearine to a solid fat content similar to that of barrier fat A?

Hydrogenating sunflower oil itself to such a solid fat content required a slip melting point of about 38°C - a product which we shall call SF38. This had a permeability which was higher than that of barrier fat A. Adding the 50% sunflower wax concentrate to this at levels of 5% and 10%, however reduced the permeability to the kinds of levels found when it was added to barrier fat A.

Partially hydrogenating the sunflower stearine to the same solid fat content - a product which we shall call SFs38 - resulted in permeabilities of between 0.46 and 1.09 from various pilot-plant and factory-scale hydrogenations (Figure 12). This, then, is not only a significant improvement over what can be achieved by triglycerides alone it is also a great improvement over what can be achieved by simply blending the more commonly known vegetable waxes with a triglyceride system.

Figure 12

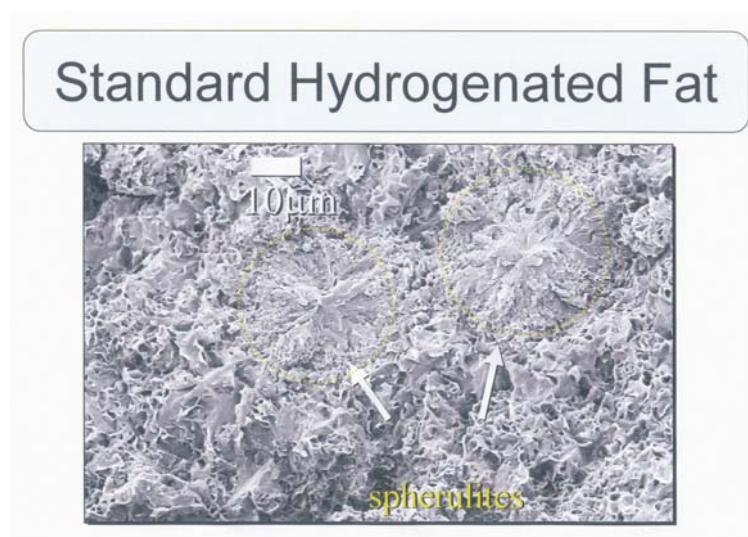
### Addition of SF wax concentrate to barrier fat A and SF38



The question then is - why is this system so good in terms of its permeability? The answer can be found in the crystal structure. As we hypothesised, increasing the tortuosity within the barrier layer will reduce the permeability.

If we look at a scanning electron microscope photograph (Figure 13) of a partially hydrogenated vegetable oil then we can see that the fat has a tendency to crystallise as spherulites.

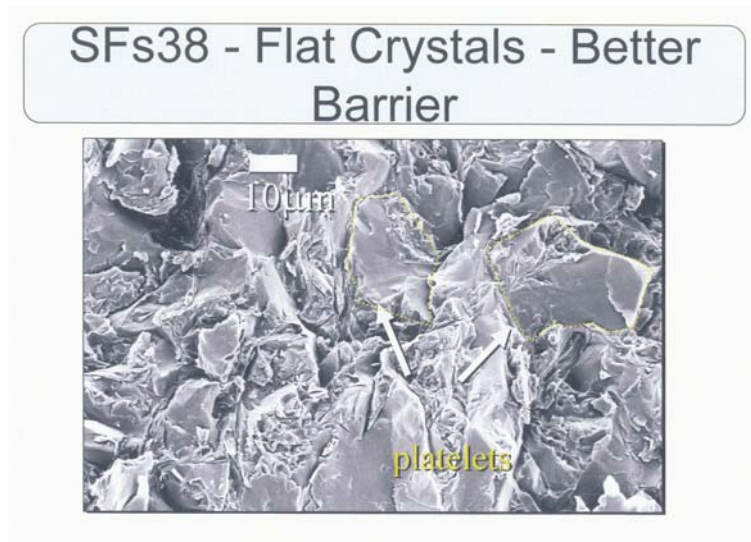
Figure 13



If, however, we look at the scanning electron microscope photograph of SFs38 (Figure 14), then we can see clear differences and the presence, not of spherulites, but of plate-like crystals. SFs38 is a partially hydrogenated vegetable oil with about 6% sunflower wax esters present. The presence of these wax esters has made all the

difference in terms of its crystal structure, in terms of its tortuosity, and in terms of its permeability.

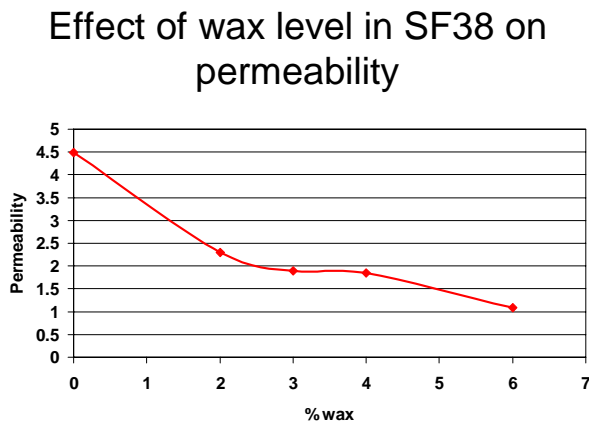
Figure 14



The permeabilities of 0.46 up to 1.09 which were found in different batches of the sunflower stearine barrier were all obtained on systems containing about 6% wax esters.

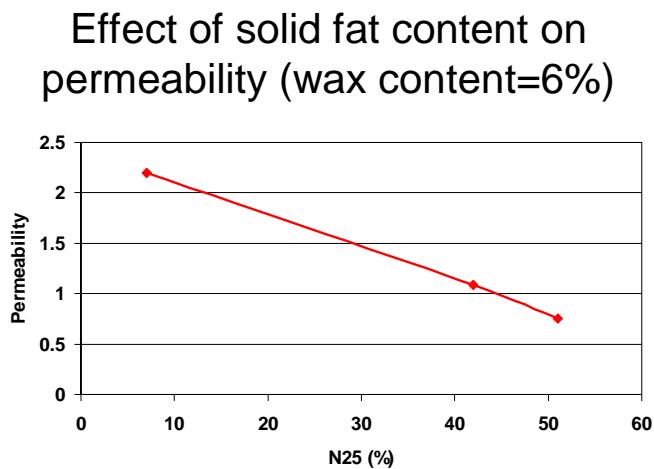
By blending the highest permeability example of these with SF38, i.e. the corresponding system without any concentration of the waxes we can see the effect that the wax level has on permeability (Figure 15). Apart from a slight plateau effect between 3% and 4% wax there is a general decrease in permeability as the wax content increases.

Figure 15



The effect of solid fat content on permeability has already been referred to and we can demonstrate the effect of solid fat content in this system by blending the hydrogenated sunflower stearine with unhydrogenated sunflower stearine, both with wax levels of 6%. The effects on permeability are as shown in Figure 16. To achieve permeabilities below 1 an N25 of greater than 45% is needed.

Figure 16



Instrumentally measured permeabilities are one thing; actual application in a real food system can be something totally different. So how does the sunflower stearine barrier perform in reality?

The first thing to note about such a fat/wax system is its melting point. This is 68°C. First thoughts are that this would be noticeably waxy when consumed in a food product. Such concerns can be dispelled by the fact that the amount likely to be used is very small because barrier layer thicknesses of about 250 microns would be the norm. At this loading, when consumed with the rest of the product the high melting point would not be noticed. Indeed such high melting points are not unusual for waxes, including those already used in foods with both beeswax and candelilla wax having comparable melting points. Carnauba wax has a considerably higher melting point at 82-86°C, a melting point which would necessitate application temperatures approaching 100°C!

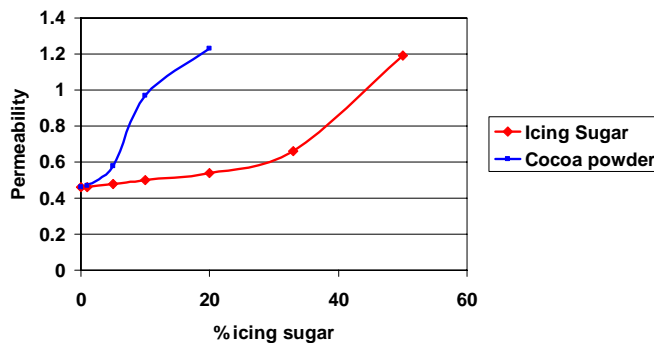
A melting point of 68°C does, however, mean that the system would need to be applied as a barrier at a temperature of about 80°C. This does have certain implications, firstly for health and safety in terms of spraying a lipid system at such a high temperature, and secondly, in terms of ensuring that the fat/wax system is kept molten throughout the spraying equipment. If this is not done, then spray nozzles can easily block as the fat solidifies in the spray units. Fortunately, the major manufacturers of spray equipment can now supply nozzles which have integral heating systems to prevent such blocking.

The second thing to consider is whether the inclusion of any non-lipid material within the barrier would be beneficial or detrimental. When looking at barriers based solely on triglycerides there is, in many cases, a benefit in adding non-fat solids as inclusions. For example, the addition of 50% icing sugar to barrier fat A reduces its permeability from 3.8 to 0.74. Indeed the addition of sugar has been shown to be beneficial in terms of barrier properties with many triglyceride-based barrier fats. Not all non-fat solids act in the same way and, for example, the addition of cocoa powder to make the barrier layer look 'chocolaty' can sometimes be detrimental. Clearly these additions need to be linked with the way in which the fat crystallises. In a spherulitic hydrogenated vegetable fat system sugar is, in many cases, beneficial.

With the hydrogenated sunflower stearine system, however, the effect is entirely opposite. In this case, the addition of 50% icing sugar more than doubles the permeability rather than considerably decreasing it (Figure 17). The reason for this is most likely to be that the integrity of the platelet network is being adversely affected by the presence of particles of sugar.

Figure 17

### Effect of non-fat solids on the permeability of SFs38

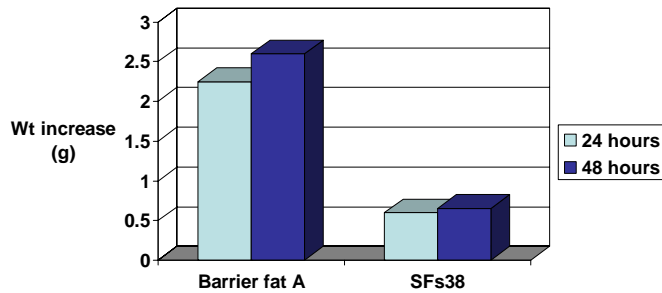


A similar effect was observed when cocoa powder was added with only 20% cocoa powder being needed to give the same increase in permeability as was observed with 50% icing sugar.

To get back to my earlier question - how does the sunflower stearine barrier perform in reality? The answer is - very well. A quick and easy test of the barrier is to take commercially pre-baked pastry shells with an outer foil cup and coat these with the barrier. These shells were then filled with a fruit and gelatine mix and the weight increase of the pastry measured over a 48 hour storage period. Most of the moisture migration occurs in the first 24 hours after which an equilibrium of sorts is reached (Figure 18).

Figure 18

## Comparison of barriers on pastry shells



But a real picture is worth a thousand words, so, in summary, I leave you with a photograph (Figure 19) showing, on the left, a pastry tart protected with the sunflower stearine fat/wax barrier and, on the right, a similar pastry tart protected with a simple hydrogenated fat barrier. Both had been stored at 5°C for 5 days.

Figure 19



In closing I would like to acknowledge the contribution made to this work by a number of people in Loders Croklaan and Unilever Research:

- to Kevin Smith, Ian Chandler, Kevin Dilley and Chris Cawthorne at Unilever Research
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