

## Hydrophobic Films and Their Efficiency against Moisture Transfer. 2. Influence of the Physical State

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Moisture transfer has been studied in a system composed of a support (cellophane) and a coating material containing different proportions of a solid phase (paraffin wax or *n*-octacosane) mixed with a liquid one (paraffin oil or *n*-hexadecane). In the test conditions (25 °C, 22–84% RH, and 45 ± 6 g of hydrocarbon/m<sup>2</sup>) a significant increase in permeability of the coated film was obtained for mixtures containing less than 25% solid. Different structural features were established which explain the difference in permeability: orientation, length, and size and shape of the aliphatic chains. The actual proportions of *n*-alkanes and the presence of the two phases were verified. Results suggest that liquid lipids up to 75% may be used to improve coating performance of solids without diminishing their moisture barrier properties.

### INTRODUCTION

The protection of foods against their environment until consumption is becoming one of the most important preoccupations in food preservation. Water is one of the factors that influence the stability. The water migration between the product and its surrounding atmosphere may be responsible for a modification of texture and appearance; different solutions have been proposed (Labuza and Breene, 1989).

Nature has solved this problem; for example, plant cuticles can be considered natural moisture membranes. Leaves and fruits are covered with films containing waxes and structural polysaccharides. This thin layer of wax, ranging from 2 to 5 μm, determines water-repellent properties, thus diminishing water loss and preserving the leaf or fruit internally. The removal of the wax contained in plant cuticles decreases the efficiency of this natural membrane by 350–500-fold (Schönher, 1976a,b; Biquet, 1987). Bain and McBean (1967) have studied the role of composition and structure of the natural wax layer present in prune plums on the rate of water loss when these fruits are dried. Any treatment disturbing the surface structure of this layer, such as abrasion, increases the moisture exchange, and the time of drying is diminished.

Edible films, defined as thin layers of materials which may be eaten by the consumer, provide a barrier to mass transport in or through fresh and manufactured foods. They are used to increase protection of the foods against the environment (Guilbert, 1986). They can also be used to limit water transfer between two parts of a product with different water activities (Kamper and Fennema, 1985; Biquet and Labuza, 1988; Kester and Fennema, 1989a).

Hydrophobic substances such as lipids have been shown to have a higher efficiency than polysaccharides or proteins and some synthetic materials such as polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride) (Kester and Fennema, 1986; Guilbert and Biquet, 1989). Lipids, however, do not form a film; they must be associated with a film-forming agent such as proteins (Torres et al., 1985), cellulose ether (Kester and Fennema, 1989b), or LM-

pectins (Schultz et al., 1949). These substances can be mounted over a support, and their coating efficiency tested (Kester and Fennema, 1989c; Martín-Polo and Voilley, 1990).

Lipids have different physical states depending on their chemical composition, structure, and molecular weight. At room temperature they can be liquid or solid. The performance of solid lipids to retard the movement of water has been pointed out in the literature and may depend on the method used to make the films or coatings.

Fox (1958) showed for wax-coated cellophane that the efficiency of paraffins depends on the size and number of paths around the crystallites. Any conditions that produce larger and closer packed plate crystals oriented parallel to the plane of the base sheet will tend to reduce the transfer. An increase in the working temperature (23–35 °C) and the length of storage (5–35 days) induces healing and recrystallization, which increases the efficiency against moisture transmission.

Landmann et al. (1960) observed a 300-fold increase in the efficiency as the content of hydrogenated cottonseed oil in nonhydrogenated cottonseed oil ranged from 40 to 100%.

Kamper and Fennema (1984) showed that if the degree of saturation of the lipid increased, the barrier properties also increased; paraffin and beeswaxes were more resistant than polyunsaturated corn oil for films prepared according to an emulsion technique. They suggested that the large difference in permeability between liquid and solid lipids could be explained in terms of the water-vapor solubility in the liquid phase and/or on the molecular organization of the lipid.

Kester (1988) pointed out that two factors significantly affect oxygen and water-vapor permeability: the type of lipid chosen, especially its solid-state morphological characteristics (intra- and intercrystalline arrangement or polymorphism) and the relative polarity of the support, whose water-vapor sorption can mask the efficiency of the hydrophobic material.

In a previous study we investigated the influence of the preparation technique over the efficiency against moisture transfer through hydrophobic films (Martín-Polo et al., 1992). We observed that for the same content of paraffin (oil or wax) the differences in limiting the water-vapor transfer were related to the final repartition of the

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**Table I. Characteristics of Pure *n*-Alkanes and Paraffins**

material	MW	purity, %	mp, °C	density at 25 °C, g mL <sup>-1</sup>
pure <i>n</i> -alkanes				
<i>n</i> -hexadecane (C <sub>16</sub> H <sub>34</sub> ) (Fluka)	226.45	>98	15.6	0.77
<i>n</i> -octacosane (C <sub>28</sub> H <sub>58</sub> ) (Fluka)	394.77	>98	65.0	0.78
paraffins				
paraffin oil (Merck)			-16.5	0.88
paraffin wax (Merck)			70-74	0.87

**Table II. Means and Standard Deviations of Film Thickness as a Function of the Solid Proportion for Both Types of Hydrophobic Substances<sup>a</sup>**

solid proportion, %	thickness, ×10 <sup>-6</sup> m	
	paraffins	<i>n</i> -alkanes
0	80 ± 10	80 ± 15
5	70 ± 10	
10		60 ± 10
25	60 ± 15	80 ± 15
50	80 ± 10	70 ± 10
100	70 ± 10	100 ± 10

<sup>a</sup> Means are obtained from five measurements of at least three films for each solid proportion.

hydrophobic material in the film or over its surface. Films with a dispersed repartition of the hydrophobic material had poor barrier properties compared to films having a continuous coated layer. A dispersed repartition is due to differences in polarity between the support and the hydrophobic material (emulsion technique) or in the porosity of the support (dipped W-111 filter paper in paraffin oil or in molten paraffin wax).

In the same study, we have also encountered a marked difference in efficiency between the liquid and solid paraffin, particularly for the dipped cellophane films.

As an attempt to explain the mentioned behavior, the objective of the present work is to study the barrier properties as a function of the physical state of hydrophobic films made of solid-liquid mixtures by differential scanning calorimetry (DSC) as well as their structural morphology by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

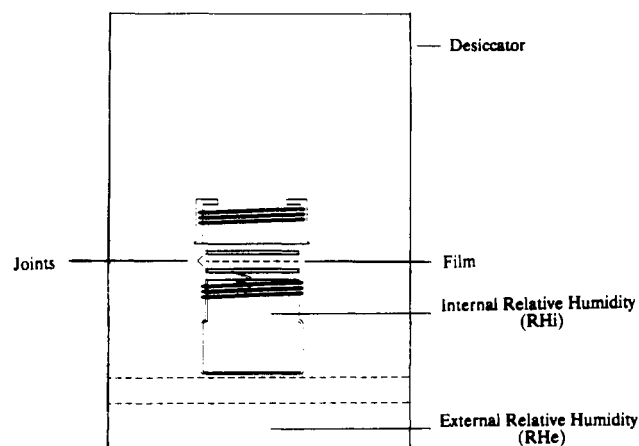
## MATERIALS AND METHODS

Two types of hydrophobic substances were studied: pure *n*-alkanes and paraffins (Table I). Paraffin oil and *n*-hexadecane are in the liquid state; paraffin wax and *n*-octacosane are in the solid state. Their water contents, as determined according to the Karl Fischer method, were less than 1.0%.

The solid-liquid mixtures, expressed as the proportion of the added solid material (% w/w), were 0, 10, 25, 50, and 100% *n*-octacosane (*n*-C<sub>28</sub>H<sub>58</sub>) in *n*-hexadecane (*n*-C<sub>16</sub>H<sub>34</sub>) and 0, 5, 10, 25, 50, and 100% paraffin wax in paraffin oil.

**Film Preparation.** The support (cellophane 300P, Courtaulds Films) was equilibrated over P<sub>2</sub>O<sub>5</sub> at room temperature prior to its being dipped into a solution of the molten hydrophobic material which was diluted in hexane (40% w/w), at 65 °C for pure *n*-alkanes and at 74 °C for paraffins, and then drained for 1 min. Dipping of the cellophane in the pure liquids was carried out at room temperature. Before the water vapor transmission rate (WVTR) was tested, the weight of the coated films was recorded to ensure complete evaporation of the solvent (24 h). The quantity of hydrocarbon deposited over the cellophane was determined by weighing the cellophane disks (3.5-cm diameter) before and after coating. This quantity was controlled and fixed at a constant value of 45 ± 6 g of hydrocarbon/m<sup>2</sup> of film.

Thickness was measured with a micrometer (0.01 mm) at five locations on the film. For the liquid films, thickness was calculated as previously described (Martín-Polo et al., 1992) (Table II).



**Figure 1.** Glass permeation cell used for the measure of the water vapor transmission rate. The glass permeation cell is 3.4 cm (i.d.) by 5.4 cm (o.d.) by 3.4 cm deep, with an exposed film area of 9.1 cm<sup>2</sup>.

**Measurement of the Water Vapor Transmission Rates (WVTR).** The WVTR of the films was determined gravimetrically at 25 °C according to AFNOR (1974) procedure NF H00-030. The film was sealed in a glass cell as described previously (Martín-Polo and Voilley, 1990) (Figure 1). The glass cell contained a saturated salt solution of potassium acetate (Merck), giving an internal relative humidity of 22.6% (RH<sub>i</sub>). The cell was placed in a desiccator containing a saturated salt solution of potassium chloride and maintained at an external relative humidity of 84.3% (RH<sub>e</sub>) (Merck).

The water vapor permeability (WVP) was calculated from the WVTR as

$$\text{WVTR} = \Delta w / \Delta t A \text{ (g m}^{-2} \text{ s}^{-1}\text{)} \quad (1)$$

$$\text{WVP} = (\text{WVTR})l / (p_1 - p_2) \text{ (g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}\text{)} \quad (2)$$

where  $\Delta w / \Delta t$  is the amount of moisture gain per unit time of transfer (g s<sup>-1</sup>),  $l$  is the film thickness (m),  $A$  is the area exposed to moisture transfer (m<sup>2</sup>),  $p_1$  and  $p_2$  are the vapor pressures of water on either side of the film,  $(p_1 - p_2)$  is the driving force (Pa), and  $P$  is the water vapor permeability (g m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>).

Each solid proportion was done in triplicate, and two disks were tested each time. The cells were weighed daily.

**X-ray Diffraction (XRD).** The crystalline structures of films coated with both liquid and solid hydrophobic substances in two proportions were studied by analysis of the XRD patterns at room temperature. To verify that crystalline morphology did not change either during the WVTR measures or with the high RH, we recorded XRD patterns of films before and after 10 days of storage at 84% RH and over P<sub>2</sub>O<sub>5</sub> at room temperature. Copper radiation ( $\lambda = 1.54056 \text{ \AA}$ ) and curved position-sensitive detector CPS 120 INEL were used.

**Scanning Electron Microscopy (SEM).** Surface morphology of the dipped films for both material types was observed and compared to that of the solid proportion in the mixture. A JEOL JSM-35CF (JEOL Ltd., Tokyo) scanning electron microscope was used. Pieces of film (5 mm<sup>2</sup>) were mounted on copper stubs, fixed with double-sided tape, and then coated with gold. A 15-kV accelerating voltage was used with the electron beam directed perpendicularly to the film surface. Micrographs were taken at room temperature.

**Differential Scanning Calorimetry (DSC).** Thermal analysis was carried out only for mixtures of pure *n*-alkanes. Samples for DSC were prepared for the different solid proportions of *n*-octacosane in *n*-hexadecane by scraping off the coating material of the dipped cellophane. A fixed quantity (2-7 mg) of the coating material was introduced into aluminum pans which were hermetically sealed and placed in a Perkin-Elmer 2C differential scanning calorimeter. Measurements were recorded using an empty pan as reference; the heating rate was fixed at 10 °C/min.

## RESULTS AND DISCUSSION

**Water-Vapor Transfer.** Curves of the whole cell weight gain vs time (148 h of transfer) are all straight lines ( $r^2 = 0.998$ ) for coated and uncoated cellophane. The WVTR and WVP calculated from the slopes of these curves will be discussed separately for each type of hydrophobic material. The variation coefficient for the WVTR measurements was 13–22%. Concerning the behavior exhibited for the *n*-alkanes, when the solid proportion passes from 0 to 25%, the WVP decreases sharply from  $15.8 \times 10^{-11}$  to  $0.44 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ . In going from 50 to 100%, permeability increases slightly, from  $0.52 \times 10^{-11}$  to  $6.87 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ . This abnormal behavior will be discussed further in light of the results from SEM and XRD.

The behavior exhibited by paraffins for WVP is  $11.27 \times 10^{-11}$  and  $0.10 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  in the liquid and solid states, respectively. The latter limits 100-fold the moisture transfer compared to the liquid paraffin. For all of the other solid proportions (5, 10, 25, and 50%), neither the WVTR nor the WVP differs significantly.

In the AFNOR method we have used, the WVTR calculated from the weight gain of the whole cell accounts for the water vapor in the film and the water vapor already transferred. In this method no distinction can be made to determine if the water vapor has actually been transmitted. We can only calculate an apparent permeability.

As an attempt to understand why the different proportions of paraffin wax had the same WVTR and WVP, we followed the weight evolution of the saturated salt solution: the RH<sub>i</sub> compartment (Figure 1). The WVP calculated from the weight of the saturated salt solution accounts only for the water vapor really transmitted and is called true permeability.

We proceeded as follows: at time zero, eight cells for each type of film preparation were introduced in the desiccator at 84.3% RH (RHe). Two cells were taken out after 2, 5, 7, and 10 days of transfer. The weight of both compartments, the film on its own, and the saturated salt solution were recorded separately.

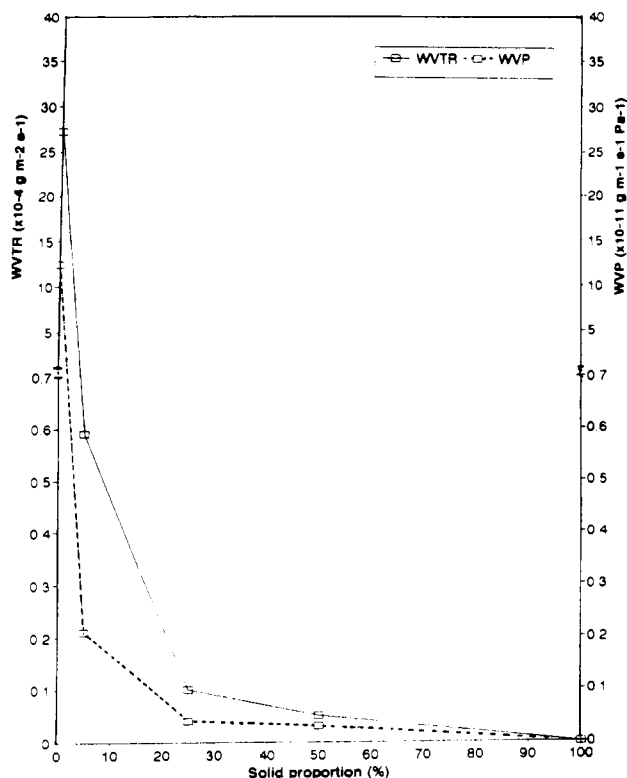
The results of this experiment showed that the amount of water actually transmitted decreases as the paraffin wax proportion increases (Figure 2). Values given are obtained after 7 days of transfer. This behavior was not observed for the *n*-alkanes; the weight gain of the saturated salt solution is higher for the pure solid material compared to that of the other solid proportions (Figure 3).

The barrier properties of the *n*-alkanes are less than those of the paraffins. However, in both films an increase in the true permeability is observed if the solid proportion is lower than 25%.

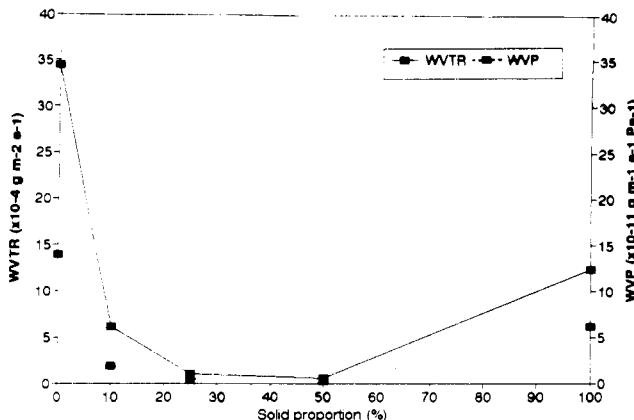
**Scanning Electron Microscopy and X-ray Diffraction.** In an attempt to elucidate the role of the film structure in the resistance against moisture transmission, SEM and XRD were used to characterize the surface of coated cellophane films of different solid proportions.

The films composed of the pure liquids (paraffin oil or *n*-hexadecane) were not observed by SEM. Only large diffusion peaks were observed on XRD patterns for both substances.

**Paraffins.** SEM on the films containing paraffin wax showed a relatively uneven but smooth continuous surface. No individual crystals or platelets could be discerned, even when magnification was increased up to  $\times 1000$  (Figure 4). X-ray analysis proves that the wax is actually crystallized as illustrated by the pattern shown in Figure 5: the planes (*hk*0), (*h*00), and (0*k*0) are present in the XRD patterns. The strong diffraction lines at  $d = 4.13$  and  $3.73 \text{ \AA}$  can be



**Figure 2.** WVTR and WVP for paraffins from the weight gain of the saturated salt solution as a function of the solid proportion (7 days of transfer at 25 °C and 22–84% RH).



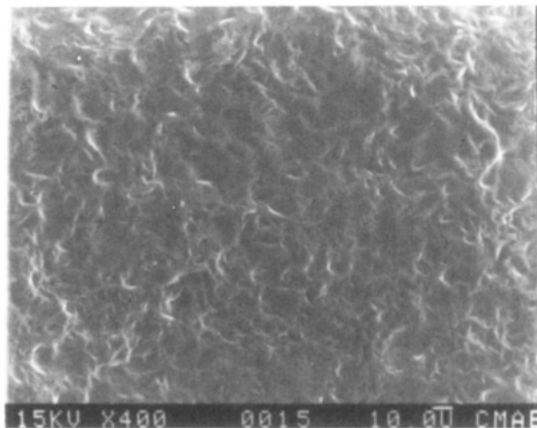
**Figure 3.** WVTR and WVP for *n*-alkanes from the weight gain of the saturated salt solution as a function of the solid proportion (7 days of transfer at 25 °C and 22–84% RH).

indexed as planes (110) and (200) of an orthorhombic cell whose parameters are  $a = 7.45 \text{ \AA}$  and  $b = 4.96 \text{ \AA}$ , as reported by Edwards (1958).

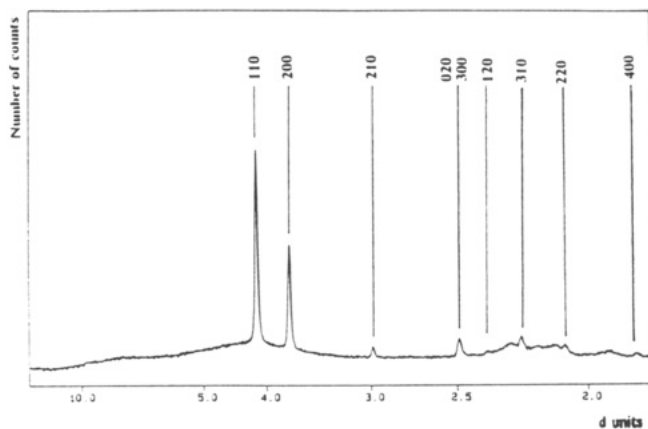
The fact that (00*l*) and (*hkl*) planes with  $l \neq 0$  do not diffract means that the long aliphatic chains are parallel to the base sheet of the cellophane or that the aliphatic chains have different lengths.

Our results are in agreement with those of Fox (1958) concerning the structural characteristics of 100% paraffin wax coated cellophane and the relation with its high efficiency to limit moisture transfer as explained by the parallel orientation of the crystals to the base sheet of cellophane.

The presence of liquid material (paraffin oil) does not influence the orientation of the crystals (as proved by the XRD patterns in Figure 6) or their surface (as seen by SEM). In fact, it acts as a diluant; i.e., the crystal proportion decreases so the paths between crystals are



**Figure 4.** Electron micrograph of coated cellophane with paraffin wax (100%) viewed from the coated surface. Amount of hydrophobic material per area unit of cellophane is  $45 \pm 6 \text{ g m}^{-2}$  ( $X \pm \text{SD}$ ). Micrograph was taken with electron beam directed normal to the film surface. White bar represents  $10 \mu\text{m}$  in length.



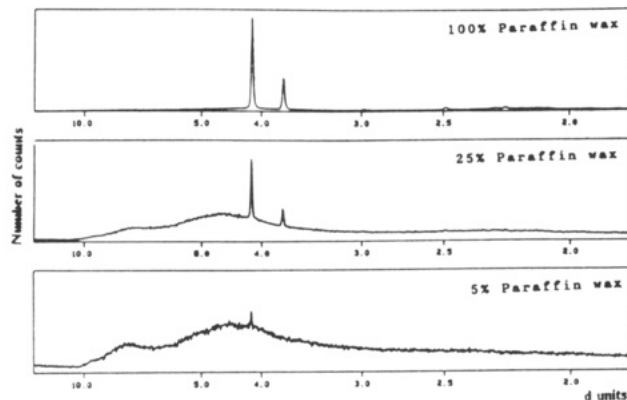
**Figure 5.** X-ray diffraction patterns of 100% paraffin wax. Lines are indexed in an orthorhombic cell (parameters are indicated in the text). Diffraction spacings are in  $d$  units ( $\text{\AA}$ ).

more and more numerous for water-vapor molecules to pass through as the liquid phase increases. This dispersed phase is not as efficient as a continuous solid layer of 100% paraffin wax. These results confirm the role of the distribution of hydrophobic material as pointed out previously (Martín-Polo et al., 1992).

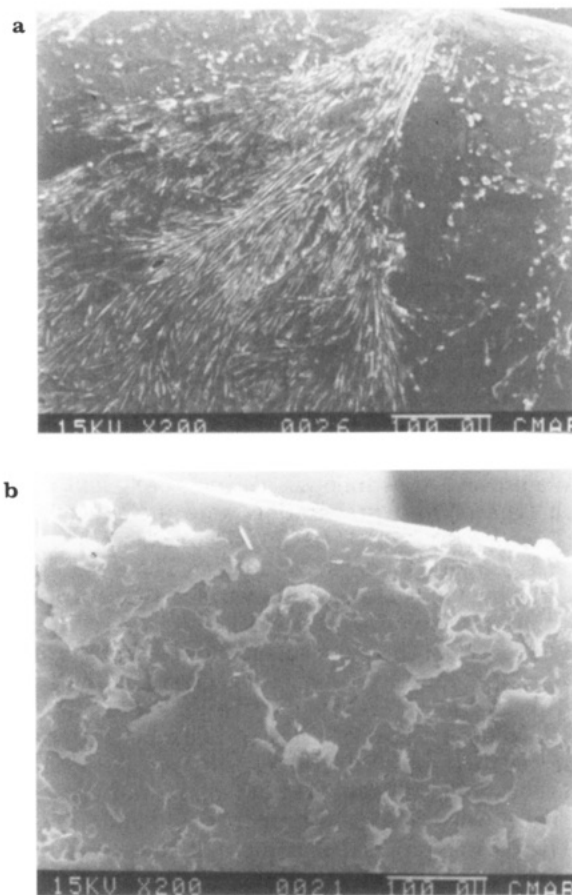
A significant increase in the moisture transfer was obtained when the paraffin wax amount was lower than 25%. This means that the quantity of crystals is so low that it does not cover the cellophane surface.

**Pure *n*-Alkanes.** SEM of the films containing pure *n*-alkanes showed individual crystals. The arrangement is different according to the *n*-octacosane proportions; for 100%, clusters of needles are observed, while stacking of separated flakes is seen for 10% (Figure 7). From the XRD pattern (Figure 8) of the 100% *n*-Octacosane, an orthorhombic cell having the following parameters, as reported by Boistelle et al. (1976), can be assigned:  $a = 7.42 \text{ \AA}$ ,  $b = 5.59 \text{ \AA}$ ,  $c = 66.5 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . Furthermore, a different arrangement of the aliphatic chains is observed, which could be related to the existence of needle clusters as shown in Figure 7. For 25% or lower proportions of *n*-octacosane, only diffraction lines corresponding to the plane (00 $l$ ) are represented; in this case the unique observed orientation for the aliphatic chains is perpendicular to the base sheet of the cellophane (Figure 8).

Our WVTR results for the coated film with 100% *n*-octacosane characterized by a heterogeneous or porous structure are in agreement with those of Kester and Fen-



**Figure 6.** X-ray diffraction patterns of paraffin coated films as a function of % (w/w) of paraffin wax mixed with paraffin oil. Diffraction spacings are in  $d$  units ( $\text{\AA}$ ).



**Figure 7.** Electron micrographs of coated cellophane films with pure *n*-alkanes as a function of the solid content (% w/w) as viewed from the coated side. Amount of hydrocarbon is  $45 \pm 6 \text{ g m}^{-2}$  ( $X \pm \text{SD}$ ). Micrographs were taken with electron beam directed normal to the surface. (a) 100% *n*-octacosane; (b) 10% *n*-octacosane in *n*-hexadecane. White bars represent  $100 \mu\text{m}$  in length.

nema (1989c) for films of *n*-hexatriacontane, showing a low barrier efficiency against moisture transfer because of their "porous" structure.

The abnormal behavior of the 100% *n*-octacosane against moisture transfer observed with respect to the 50, 25, and 10% solid can be explained by the different shape and size of the crystals as well as the chain orientations. Indeed, the morphology of the 100% *n*-octacosane film contains void regions (transfer of moisture only through cellophane), while for all of the other films with another proportion of solid the liquid material (*n*-hexadecane) fills

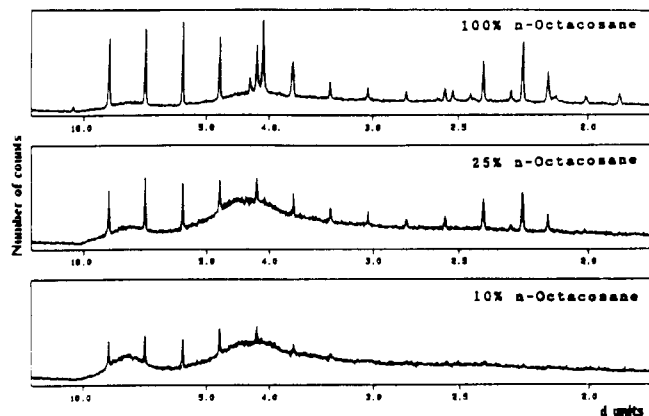


Figure 8. X-ray diffraction patterns of pure *n*-alkanes of coated cellophane films as a function of % (w/w) of *n*-octacosane mixed with *n*-hexadecane. Diffraction spacings are in *d* units (Å).

Table III. Real Proportions of *n*-Octacosane Mixed with *n*-Hexadecane Calculated from DSC Measurements<sup>a</sup>

$\Phi_g$	$\Delta H_f$ , J/g	melted proportion of <i>n</i> -octacosane	$\Phi_m$	100 - $\Phi_m$
100	250	100		
80	194	77.6	98.5	1.5
71	172	68.8	98.3	1.7
50	119	47.6	97.6	2.4
25	44	17.6	95.2	4.8
10	17.4	7.7	87.7	12.5

<sup>a</sup> Heating rate was 10 °C min<sup>-1</sup>.

the void spaces between crystals and produces greater resistance to the passage of the water molecules.

**Differential Scanning Calorimetry.** Using thermal analysis, we verified the constancy of composition and structure of prepared dipped cellophane films for both types of hydrophobic substances.

In light of the interpretation of the thermograms for the paraffins, broad peaks, solid–solid phase transitions (Craig et al., 1968), this part of the study was carried out only with pure *n*-alkanes, corresponding to the major components encountered in paraffin wax and oil (Edwards, 1958; Lawrence et al., 1982; Lawrence and Iyengar, 1983). We suspect that similar behaviors may occur in mixtures of paraffins.

We observed that the solvent used to prepare the films produced slight decrease in the onset and maximal melting temperatures (3–4 °C) as compared to the thermal behavior of the molten mixtures without solvent.

Concerning the storage conditions at different relative humidities (84.3% and P<sub>2</sub>O<sub>5</sub>), there was no modification in the thermal behavior of the coating mixtures.

The DSC analysis allows us to verify the real proportions of the materials tested in water-vapor transmission (Table III) and to establish the phase diagram of the *n*-octacosane in *n*-hexadecane mixture, showing the presence of each phase (solid and liquid) in all of the studied proportions at 25 °C (Figure 8).

Concerning the proportion of *n*-octacosane in *n*-hexadecane, we observed that the calculated solid proportion from the enthalpy change of the *n*-octacosane melting is lower than the added amount when preparing the films.

This difference may be due to a partial solubilization of *n*-octacosane in the *n*-hexadecane. We estimated the fraction of *n*-octacosane remaining solid by eqs 3 and 4, assuming that the mixture follows an ideal solubility behavior (McClements and Povey, 1988)

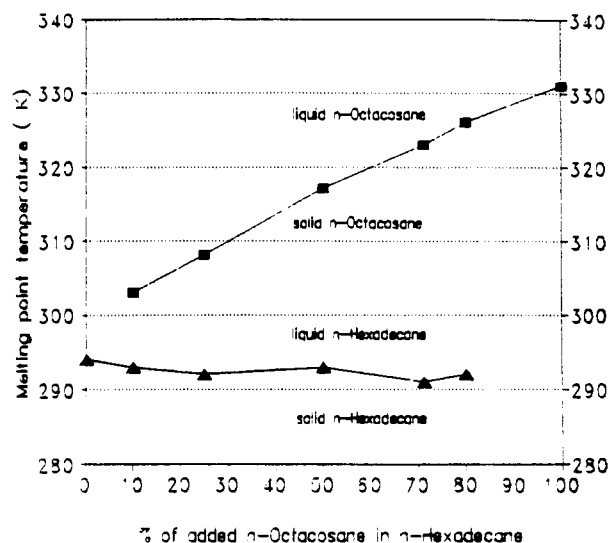


Figure 9. Binary phase diagram of *n*-octacosane mixed with *n*-hexadecane forming a system with partial miscibility.

$$\ln X = \frac{\Delta H_f}{R} M_w \left( \frac{1}{T_{mp}} - \frac{1}{T} \right) \quad (3)$$

where  $X$  is the mole fraction of *n*-octacosane in the liquid phase,  $\Delta H_f$  is the enthalpy change per mole of crystallized material,  $R$  is the gas constant,  $T$  is the absolute working temperature, and  $T_{mp}$  and  $M_w$  are the absolute melting point and the molecular weight of the pure *n*-octacosane, respectively.

The mass fraction ( $\phi_m$ ) of the *n*-octacosane in the solid state can then be calculated from the relation

$$\phi_m = \frac{\phi_g - \frac{X(1 - \phi_g)MW}{MW_0(1 - X)}}{\phi_g} \quad (4)$$

where  $\phi_g$  is the total mass fraction of *n*-octacosane present in the mixture and  $MW_0$  is the molecular weight of *n*-hexadecane. The solubilized proportion is equal to 100 -  $\phi_m$ . This quantity increases with increasing amounts of *n*-hexadecane. This solubilization explains the lowering of the melting point of *n*-octacosane shown in the phase diagram (Figure 9).

The influence of the thermal history of the coating materials was verified by comparing the thermograms obtained from repeated heating and cooling cycles giving rise to different arrangements of crystals of *n*-octacosane, as reported in the literature. Odd-numbered hydrocarbons crystallize in an orthorhombic lattice. The lower even-numbered *n*-alkanes including *n*-C<sub>24</sub>H<sub>50</sub> form a triclinic lattice. The *n*-octacosane (*n*-C<sub>28</sub>H<sub>58</sub>) shows a solid–solid transition at a temperature near its melting point as do the odd-numbered *n*-alkanes passing from orthorhombic to hexagonal to liquid (Templin, 1956; Small, 1986).

## CONCLUSION

The two types of material compared in this study correspond to the same range of hydrophobicity. This means that solubility of water vapor in the coating material is similar and negligible. In this respect all of the differences in the barrier properties should originate in the structure of the diffusion matrix of the coating *n*-alkanes or paraffins.

Changes in the efficiency against moisture transfer are observed as the solid amount decreases from 100 to 25% for both groups, and the significant differences observed

between them have been attributed to morphological features of the diffusion matrix: *orientation* of the aliphatic chains (perpendicular to the direction of transfer for paraffins and parallel for pure *n*-alkanes); *length* of the aliphatic chains (various sizes for paraffins and a unique size for pure *n*-alkanes which induces its periodic arrangements); *size* and *shape* of the crystals (uneven surface without any well-defined morphological characteristics for paraffins and needle clusters or flakes for pure *n*-alkanes).

The role of the liquid phase depends on the morphology or type of the solid hydrophobic material. For the pure *n*-alkanes the WVTR decreases slightly from 100 to 25% of the solid material. This means that the hydrophobic liquid is able to overcome or mask the imperfections of the arrangements of the morphological solid crystals, thus retarding the moisture transfer more effectively than cellophane by filling the void spaces containing no solid material. For paraffins, WVTR remains nearly constant in the interval from 100 to 25% of the solid content.

For both substances efficiency is lost when the solid content is lower than 25%, presumably because the quantity of crystals (independent of their morphology) is no longer enough to prevent molecules of vapor to pass through the film.

The fact that WVTR remains almost constant for a large interval of variation of the solid amount suggests it may be possible to overcome the problem of the rigidity of solid materials like edible waxes by using liquids to improve their flexibility and adhesiveness and to heal food imperfections without modifying their barrier properties, especially when with films formed in place (coatings) are used.

Further research must be carried out with edible mixtures of liquid–solid lipid materials to verify if similar structural features like those found in the present work are still responsible for the water barrier properties of materials having different hydrophobicities.

#### ACKNOWLEDGMENT

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