A new in vitro method for the measurement of the water vapor permeability of films has been developed to evaluate the properties of silicone. The most well-known of the commercially available silicones are the polydimethylsiloxane (PDMS) fluids. The water vapor permeability (WVP) of a wide range of PDMS materials was measured, from low-molecular-weight volatile fluids to very high-molecular-weight silicone gums. The results showed that all polydimethylsiloxanes form permeable films. This can be explained by the unique structure of the PDMS polymer.

Knowing the WVP of a material is very important. In some applications, such as suntan lotions or body milks which are applied to large areas of the body, it is desirable to have materials with high vapor permeability. One of the unique properties of silicones is their ability to formulate highly protective creams and lotions that are also permeable. In other application areas, such as facial care products, it can be an advantage to modify the permeability of an applied film so that water loss is reduced.

Pure PDMS materials are always permeable because of their structure. By adding hydrocarbon chains onto the silicone backbone, the permeability of silicones can be modified. This new family of materials, alkylmethylsiloxanes, has a permeability that can be controlled. The structural changes to the material required to achieve this are discussed in this paper. Finally, results will demonstrate the correlation between in vitro permeability testing and in vivo moisturization.

Polydimethylsiloxanes

Since the first silicone-containing skin lotion was introduced more than 30 years ago, silicones have become more important to skin care formulators. The most widely used silicones have the generic name, polydimethylsiloxanes (Figure 1).

Polydimethylsiloxanes (PDMS) consist of an inorganic siloxane backbone with pendant methyl groups. The unique structure of the silicone polymer is responsible for many of its properties. As linear polymers, PDMS are colorless fluids. They are available in a range of viscosities, depending on the chain length. At the highest molecular weight they are gum-like. Many properties are dependent on the molecular weight of the material; however, it has been shown that PDMS’ vapor permeability is independent of the molecular weight due to the unique structure of the silicones.

The rate of permeability of a gas or vapor through a material can be controlled by either solubilities or diffusion rates. From previous studies of gas permeation through silicone rubber, it was known that the unusually high permeabilities of gases in silicone rubber are mainly due to
siloxane backbone with varying degrees of substitution. The permeability of these materials was then measured using the in vitro permeability test.

**In vivo--transepidermal water loss:** After cleansing the volar forearm with mild liquid soap, each individual was equilibrated for at least 15 minutes in a room at constant temperature (25°C) and humidity (30% RH) before blank readings were taken. Skin temperatures were taken at mid-arm, and blanks were then measured at three sets of circular (2.5 cm diameter) sites laid out on parallel lines between the wrist and the elbow. Transepidermal water loss (TEWL) measurements (H$_2$O/m$^2$/hr) were made using a Servo-Med EP-1 evaporimeter; the probe was equipped with a chimney to reduce measurement drift due to air turbulence. TEWL data were collected automatically by computer. Test materials were then applied (0.0125 g with a tared glass rod) at the same sites at which blank measurements had been taken. Measurements were subsequently made at regular, specified intervals: five minutes, 30 minutes, one hour and two hours following application of the test material.

**In vivo--conductance:** Conductance was measured (in micro-ohms) using a Skicon 200 skin surface hydrometer. Five measurements were averaged for each site.

Measurements were taken under the same conditions as for the TEWL test; 0.0125 g of the test material was applied with a tared glass rod. Measurements were taken at intervals of five minutes, 30 minutes, one hour and two hours.

**Results and Discussions**

**In vitro--water vapor permeability:** Many materials have been tested in vitro using the new WVP test. The material best known for being occlusive is petrolatum. When this was measured by the WVP test, it was found to have a value of 1.25 g/m$^2$/hr. Even diluted to 40% in C$_{10-11}$ isoparaffin, the permeability was very low: 4.58 g/m$^2$/hr. For comparison, aluminium foil was tested. It was found to have a value of 0.21 g/m$^2$/hr. So, it can be seen that petrolatum is indeed completely occlusive. At the opposite end of the scale, the isoparaffin was tested and compared to collagen film to which no test material had been applied. It had a value of 148 g/m$^2$/hr, and the blank was 126 g/m$^2$/hr. Isoparaffin was tested because it was the solvent used to solubilize organics and silicones, and it was not occlusive itself.

Once the scale was set, three series of tests were performed on the following silicones:

1. Silicone materials currently used in personal care applications
2. Alkylmethylsiloxanes (AMS)
3. Blends of AMS and mineral oil

**Silicone materials:** This range of materials covers volatile silicone fluids, non-volatile fluids and high-viscosity gums. The first test was on cyclic and linear silicones. The only variable was the molecular weight. The results are shown in Table III and Figure 3.

Linear silicones are very permeable materials. Even at high molecular weights (silicone gum), they do not affect the water vapor permeability through the collagen film. It is interesting to compare these results with hydrocarbons of varying molecular weights. At low molecular weight (mineral oil) and low carbon chain length, hydrocarbons are permeable. At high molecular weight (petrolatum) and high carbon chain length, hydrocarbons are very occlusive. The molecular weight range for silicone is much larger than for hydrocarbons. A high-viscosity silicone gum can have a molecular weight of 2,000,000 compared to a molecular weight of 2366 for petrolatum. It is, therefore, very apparent that the permeability of silicones is due to the unique molecular structure of the materials, not the relative molecular size.

The high-molecular-weight silicone fluid was also tested at different application densities. In theory, a good, occlusive film-former should show a very rapid decrease in water loss with increasing application density. From the results

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>% Concentration in isoparaffin</th>
<th>Water vapor permeability g/m/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclomethicone$^*$</td>
<td>100</td>
<td>155.70</td>
</tr>
<tr>
<td>Dimethicone$^*$</td>
<td>100</td>
<td>107.40</td>
</tr>
<tr>
<td>Dimethicone$^*$</td>
<td>75</td>
<td>120.60</td>
</tr>
<tr>
<td>Dimethicone$^*$</td>
<td>30</td>
<td>142.80</td>
</tr>
<tr>
<td>Dimethicone$^*$</td>
<td>10</td>
<td>147.80</td>
</tr>
<tr>
<td>Silicone gum$^*$</td>
<td>15</td>
<td>148.60</td>
</tr>
<tr>
<td>Silicone resin$^*$</td>
<td>100</td>
<td>110.50</td>
</tr>
<tr>
<td>Mineral oil$^*$</td>
<td>100</td>
<td>98.00</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>100</td>
<td>1.25</td>
</tr>
</tbody>
</table>

$^*$DC 245, Dow Corning  
$^*$DC 200 12,500 cSt, Dow Corning  
$^*$DC 1401, Dow Corning  
$^*$DC 593, Dow Corning  
$^*$Klearol, Witco/Sonneborn

**Figure 3. Permeability of silicone materials in vitro (Payne cup)**
shown in Figure 4, it can be seen that petrolatum has the characteristic curve of an occlusive film-former. At low application density, it has a relatively high WVP (100 g/m²/hr). However, with increasing application density, this rapidly decreases to near zero water loss. Compared to petrolatum 12,500 cSt dimethicone shows very little dose-response, beginning at a water loss rate of 107 g/m²/hr and decreasing to approximately 80 g/m²/hr. The silicone resin in Table III has a three-dimensional structure; therefore, the vapor permeability is not influenced by the type of structure—linear or three-dimensional—nor the molecular weight.

**Alkylmethylsiloxanes** (AMS): An almost limitless array of linear silicone-organic hybrid compositions with the general structures in Figures 5a) and b) can be produced. The values of x, y and z, and the chain length of R, control the molecular weight as well as the hydrocarbon-to-silicone ratio in the hybrid polymers. The values of x, y, or z can range from 0 to greater than 1000. R can vary from a single hydrogen atom to C₄₅H₉₁ or longer hydrocarbon chains. Thus, three classes of materials can be produced: volatile fluids, non-volatile fluids and waxes.

1. **Volatile fluids** are typically materials with molecular weights in the range of 300 to 600 and with hydrocarbon-to-silicone ratios ranging from 0.25 to 1.00. Alkyl chain length is low. The volatile AMS are vapor permeable (see Table IV and Figure 6).

2. **Non-volatile fluids** may have molecular weights as high as 100,000; however, the R substituent is typically not longer than C₁₈H₃₇. From Table IV, it can be seen that the non-volatile fluids still have a high vapor permeability.

3. **Waxes** may range in molecular weight from 500 to 100,000, and the R substituent is typically C₁₆H₃₃ or longer. The softening points of the waxes range from 25 to 70°C. The AMS waxes have very variable permeability, as shown in Table IV.

The following general conclusions can be made:

- Short-chain alkyl groups at a low level of substitution usually results in a product with high permeability.
- Long-chain alkyl substituents are the most effective at decreasing the permeability, even at a low level of substitution.
- High hydrocarbon-to-silicone ratio is not a guarantee of high occlusivity, especially with short-chain alkyls.
- The impact of the R group on occlusivity depends on the structure of the silicone (Figure 6).
- The length of the silicone backbone chain influences the permeability to a lesser extent than the alkyl chain-length and substitution-level parameters.

In summary, the permeability of AMS depends on four interdependent factors which act on the packing density and the molecular orientations of the AMS. These factors are:

- Alkyl chain length

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**Table IV. Water vapor permeability of silicone derivatives in vitro**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Silicone chain length</th>
<th>Level of substitution</th>
<th>Water vapor permeability g/m²/hr</th>
<th>Physical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS, C₆</td>
<td>short</td>
<td>medium</td>
<td>121.0</td>
<td>Volatile fluid</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>long</td>
<td>low</td>
<td>115.0</td>
<td>Fluid*</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>long</td>
<td>medium</td>
<td>119.2</td>
<td>Fluid</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>long</td>
<td>high</td>
<td>80.6</td>
<td>Wax</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>short</td>
<td>high</td>
<td>37.0</td>
<td>Wax*</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>long</td>
<td>low</td>
<td>26.7</td>
<td>Wax</td>
</tr>
<tr>
<td>AMS, C₁₈</td>
<td>long</td>
<td>medium</td>
<td>14.2</td>
<td>Wax</td>
</tr>
<tr>
<td>AMS, C₁₆</td>
<td>short</td>
<td>high</td>
<td>6.8</td>
<td>Wax</td>
</tr>
<tr>
<td>AMS, C₁₆</td>
<td>very short</td>
<td>high</td>
<td>1.4</td>
<td>Wax</td>
</tr>
</tbody>
</table>

*All of these materials are experimental samples except as noted

*DC 5513, Dow Corning

*DC 2503, Dow Corning
the high rate of diffusion of the dissolved gases. This is due to the greater flexibility of the Si-O bond compared to the C-C or C=C bonds, which are characteristic of natural rubber. The origin of this flexibility is in the basic molecular geometry. Table I lists bond angles and bond lengths taken from a polydimethylsiloxane and the two organic systems with which the polydimethylsiloxanes are most often compared: polyethers and hydrocarbons.

In comparing silicones with natural rubber or other common polymers (e.g., polyamide, polyethylene, or polyester), the diffusivity factor is predominant. This is due to the basic molecular properties of silicones. As shown in Table I, PDMS have:

- The flattest angle and longest bond length
- Large freedom of rotation
- Many possible orientations

These properties result in high free volume, hence high permeability to gases. The large permeability values for silicones have resulted in several interesting applications (Table II).

In skin care products, the ability of silicone polymers to form a uniform, water resistant and protective, yet permeable, film on the skin is very valuable. This property is useful in protective hand creams, nappy (diaper) rash baby products and any other products where a breathable film is desirable.

**Experimental Methods**

**In vitro test—water vapor permeability:** For some time, it has been assumed that PDMS fluids are permeable, due to their inherent chemical structure. Data on silicone rubber supported this assumption. However, there was no specific data available on the fluids. Thus, an in vitro test was developed for screening potential moisturizing agents. This test was specifically designed to assess permeability. Called the water vapor permeability (WVP) test, it uses a collagen film which is spread with a thin layer of test material and placed over a cup filled with water. Weight (water) loss over time yields a rate of water loss. Thus, this in vitro test enables us to screen the permeability of many materials.

For this test, a stainless steel “K hand coater” (R.K. Print-Coat Instruments) was used to spread materials onto the substrate to a thickness of 10 microns. Previous work, as stated, had shown that the best substrate for this work was collagen. As supplied, the collagen substrate had a surface texture. The test materials were applied to this textured surface. Treated substrates (film side up) were then cut to fit over the opening of the O-ring of a specially designed, stainless steel Payne cup (Figure 2). The ring was clamped in place over the pre-warmed (31°C) lower chamber containing a specified amount of water. After initial weights were taken, the assembled cups were placed in an oven at constant temperature and humidity (31°C 12 to 18% R.H.). Weights then were taken at three points, two hours apart. Average weight losses were used to measure permeability rate (g/hr) which is the slope of the line obtained by linear regression of a weight loss versus time plot. Measurements in g/m²/hr were obtained by dividing this rate by the area of the treated substrate over which evaporation occurred. Experiments were typically run in triplicate (three cups/treatment) on two separate days.

The first materials tested using this method were the silicone fluids. Secondly, this test was used to understand how the substitution of methyl groups by other organic functionalities could affect the permeability of PDMS. In this case, a new class of organo-modified silicones was studied: alkylmethylsiloxanes (AMS). Alkyl groups of different carbon chain lengths were chemically reacted onto the
Figure 6. Water vapor permeability of Me$_3$SiO-(Me$_2$SiO)$_x$-(MeRSiO)$_y$-SiMe$_3$, the C$_{18}$, C$_{24}$ and C$_{30}$ derivatives

- Degree of substitution
- Silicone backbone chain length
- Structure

Compared to petrolatum, most AMS can be classified as semi-permeable materials.

**In vivo--TEWL and conductance tests:** These two tests are frequently used to measure skin moisturization in vivo. To be acceptable, an in vitro test needs to demonstrate a certain correlation with in vivo tests. Such correlations have been previously established, and selected examples are included in Figure 7. These results indicate a good correlation between in vivo and in vitro results. Low or negative TEWL results should correspond to high conductance and low water vapor permeability for good correlation.

When interpreting results from the in vitro test, one should be careful for the following reasons:

- Collagen is used as the support in place of the skin.
- Some materials, especially waxes, can give misleading results as there may be a physical blocking of the collagen membrane at room temperature.

But, in general, one can be confident that products showing a high permeability value in the in vitro test will not give contradictory results when tested in vivo for skin moisturization benefits.

**Conclusion**

Silicones commonly used in personal care applications are completely permeable to water vapor. But, at the same time, they form protective, water-resistant films. Incorporation of dimethicone or cyclomethicone in cosmetic products will not interfere with the skin breathability.

The permeability of PDMS can be modified by reacting hydrocarbons of different chain length onto the siloxane backbone. The permeability can be controlled by varying the degree of substitution and the length of the alkyl chain.

A decrease in permeability, by definition, means an increase in occlusivity. Highly occlusive materials, like petrolatum, are used as skin care moisturizing actives. In vivo measurements, such as transepidermal water loss (TEWL) and conductance, indicate that AMS with a reduced permeability will also increase skin moisturization. Results between in vivo and in vitro measurements show good correlation. Therefore, the water vapor permeability method is a valid in vitro screening test for moisturizing actives and formulations.

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