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Integral-Skin Foam. A Mechanism for Skin Formation

GREGORY A. CAMPBELL, *General Motors Research Laboratories, Warren, Michigan 48090*

Synopsis

Quantitative data were taken on the effect of the process variables on the skin-forming process. Analysis of these data indicates that the skin-forming process is controlled by the interaction of heat losses to the mold and increased condensation temperature of the blowing agent due to mold pressure.

INTRODUCTION

The integral-skin foam process (ISFP) produces in one operation both the low-density core foam and the high-density exterior finishable skin of molded foam parts. Since the process discovery in the fifties, many advances have been made in both chemicals and technology as described in recently published papers.[1–6] The desirability to exclude water from the system[1,3,4,6] is described, and correlations are made between water content and skin defects. Mold temperature was found to have an inverse effect on skin formation.[1,2,4,6] New mold releases were developed which provide release without tearing the skin and cleanability.[1,3,4] The effect of the thermal conductivity of the mold was reported, and it was found that although plastic and rubber molds could be used, the higher conductive metal molds were easier to control.[1,2,6] Air entrainment was found to produce skin defects. Finally, packing and the resulting pressure were found to greatly affect the skin formation.[4,6]

Several mechanisms for the skin formation have been proposed. Whitman[1] suggests that the conductive mold removes the heat that would be used to expand the blowing agent near the mold surface. Similarly, Zwolinski[3] states that heat loss to the mold prevents gas formation in the layer near the mold. Wirtz[4] argues that the increased viscosity of the foamable materials retains the blowing agent in the liquid near the mold. Then, the blowing agent escapes from the skin-forming region into the core foam to produce a compact "cell-free marginal zone." Grieve et al.[6] propose that the foam near the mold wall never blows, first, because the foam materials act as an insulator, thus promoting the center of the material to foam more readily; and, secondly, after the mold is filled, the pressure, due to packing, raises the boiling point of the blowing agent, thus keeping the foam from expanding near the mold surface.

Analysis of data taken in this laboratory indicates that these mechanisms do not explain all of the phenomena observed. This paper will present some of the laboratory data taken, and, using these data, a new mechanism will be developed. The proposed mechanism suggests that the mold is first filled with foam which has little or no skin. Then, due to a combination heat transfer to the mold and increased pressure within the mold, the skin is formed by local condensation of the blowing agent near the mold wall. The skin formation is a dynamic process continuing until either the foam gels or the pressure in the mold begins to decrease.

EXPERIMENTAL

The foam system used in this study is described in Table I. It is similar to that reported by Whitman.[1] The system was delivered using a commercial three-component, 10 lb/min machine. For each shot, the machine was calibrated to 1% in each stream and pressure balanced. The packing was controlled by the time the metering valve was open with the machine calibrated at 5 lb/min.

TABLE I
Foam Formulation

Compound 1		Compound 2		Compound 3	
Chemical	Parts by weight	Chemical	Parts by weight	Chemical	Parts by weight
E-308	91.0	E-327	9.0		
Y-6304	0.75	Dabco LV33	0.5	SF-50	32.5
Ucon 11	5.0[a]				
Ucon 113	15.0[a]				

[a] 11.8% to 16.8% by weight of foam.

The test pieces were foamed in a mold diagramed in Figure 1. The mold had dimensions of 3½ × 4 × 7 in. with a ½-in. wall. The mold temperature was varied from 80 to 160°F by placing the mold in an oven before and after filling. Core foam densities were varied from 5 to 18 lb/ft.[3] The temperatures of the foam and the mold were recorded on a Microcord Model 44 recorder. A rotary switch was placed in series with the thermocouples so that all temperatures could be recorded on the same chart. The thermocouples were selected and monitored for a minimum of 3 sec to insure an accurate reading. The mold shown in Figure 2 was used to obtain data on the effect of part thickness on skin formation. In all cases, the skin thickness was determined using a Leitz microscope at 125× magnification with a vernier slide. Electron micrographs were taken of samples of the skin and core foam. The samples were cut into ¼-in. squares and mounted on a brass slug. Then, they were vacuum coated with gold. The pictures of the surface were taken at 60× magnification, with the sample tilted 30 degrees from the horizontal.

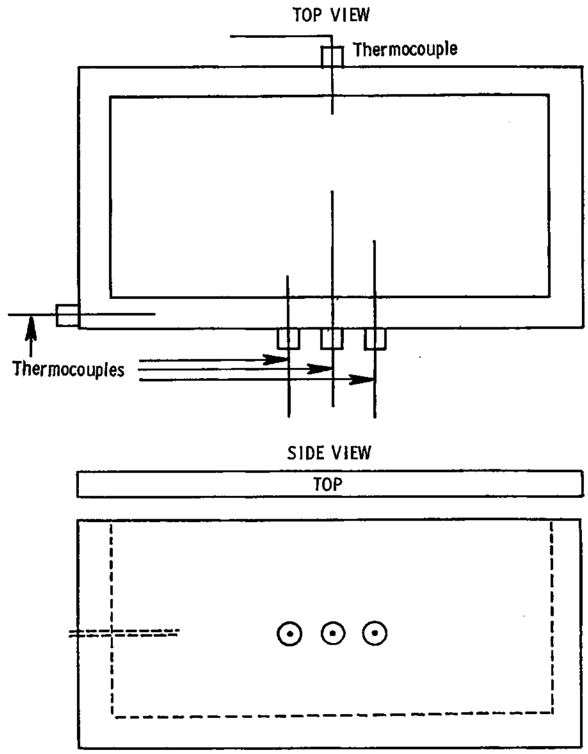


Fig. 1. Test mold.

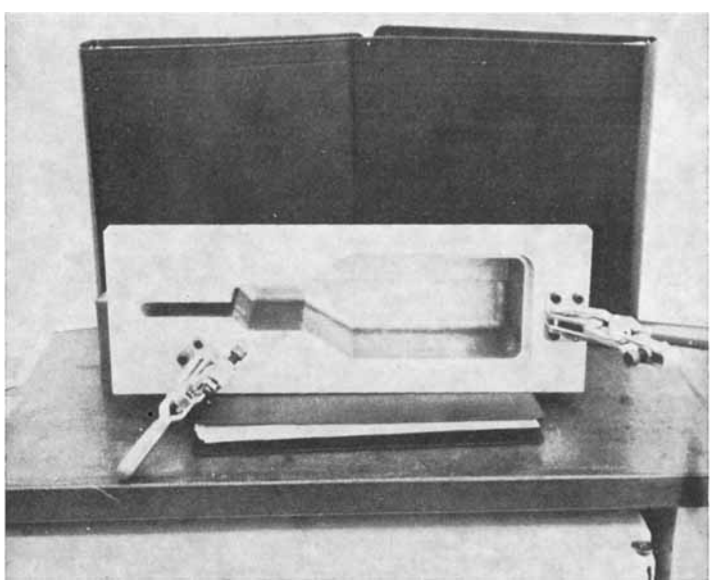


Fig. 2. Test mold.

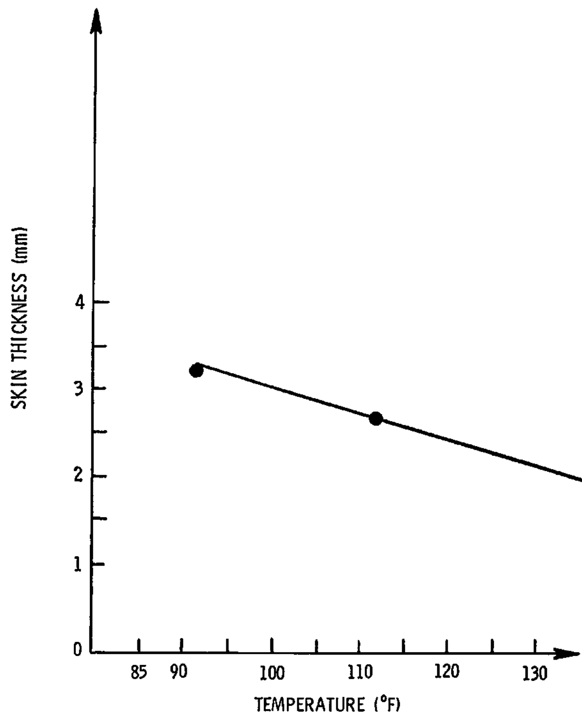


Fig. 3. Effect of mold temperature on skin formation.

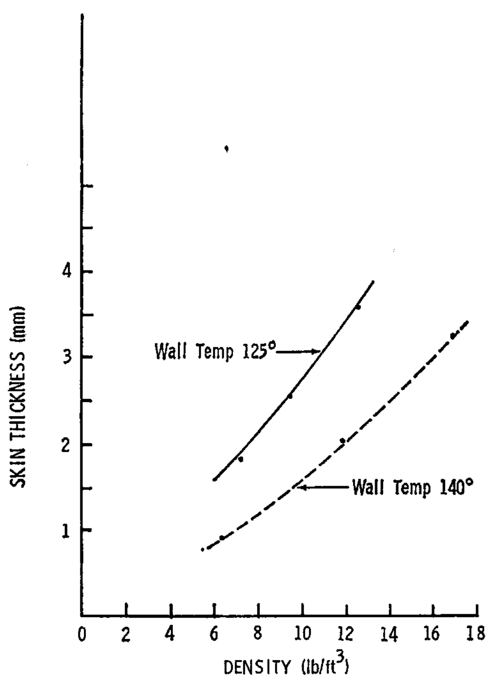


Fig. 4. Effect of mold wall temperature and density on skin formation.

RESULTS AND DISCUSSION

Variables Affecting Skin Formation

Mold Temperature. Figure 3 is representative of the effect of mold temperature on skin formation. Core density of these foams was 11 lb/ft^3. Under these conditions, 13.8% blowing agent and core density of 11 lb/ft^3, there is a linear relation between skin formation and temperature. The skin increased from 1.75 to 3.2 mm as the mold temperature was lowered from 135° to 90°F. Thus, at this core foam density, the reduction in temperature of 50°F caused about double the amount of skin to form. Wall temperature and density exhibit a nonlinear interaction on skin formation (Fig. 4). At mold temperatures of both 125° and 140°F, skin thickness was found to increase with increased core foam density. At a density of 7 lb/ft^3, the part molded at 125°F had a 1.75-mm skin, compared to 0.95 mm when molded at 140°F. At a core density of 12 lb/ft^3, the corresponding skin thicknesses were 3.4 and 2.1 mm, respectively. The 15°F increase in mold temperature resulted in a 0.8-mm reduction in skin formation at 7 lb/ft^3 density and in a 1.3-mm decrease at the higher density.

Blowing Agent. Increasing the percentage of blowing agent in the foam formulation caused an increase in skin formation. Neither the density nor

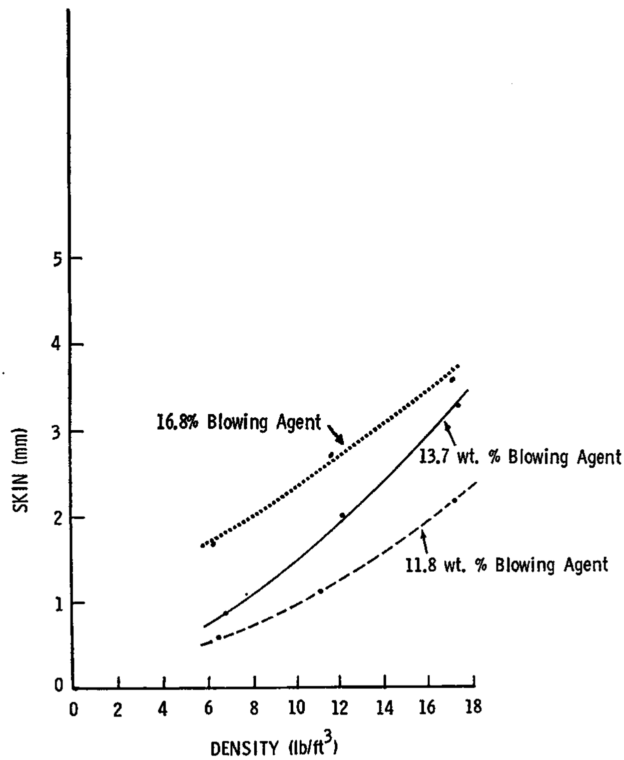


Fig. 5. Effect of blowing agent and density on skin thickness.

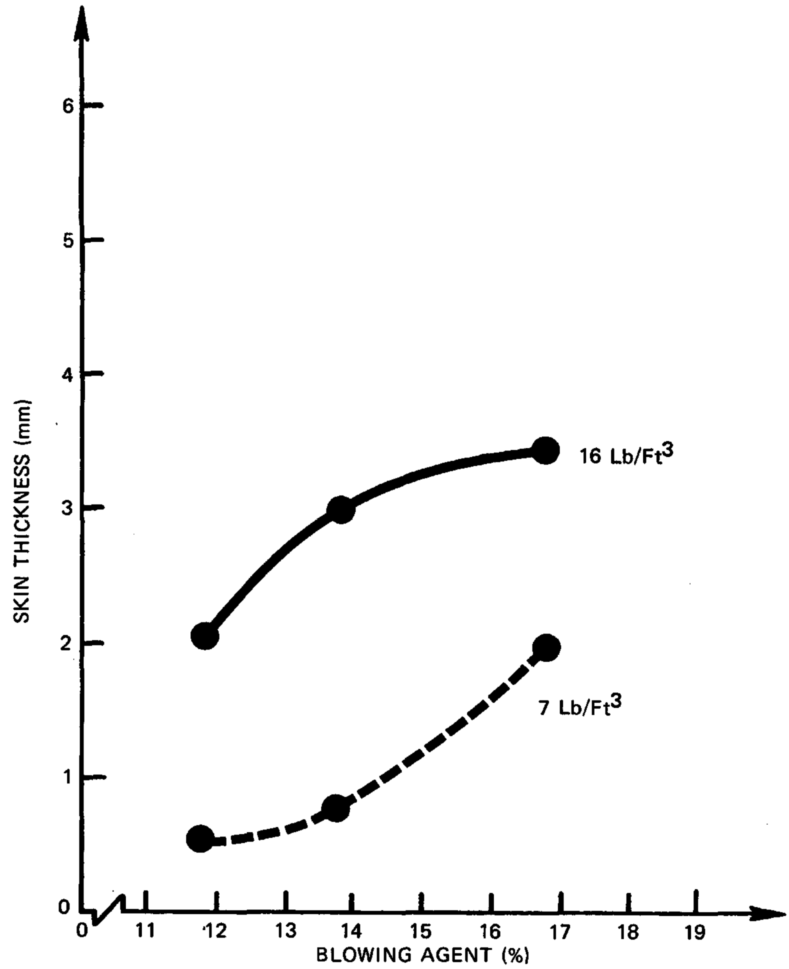


Fig. 6. The interaction of blowing agent and density on skin formation.

the per cent blowing agent has a linear effect on the skin formation (Fig. 5). The wall temperature for all samples described in this figure was 140°F. Increasing the blowing agent from 11.8% to 13.7% causes more of an increase of skin thickness at the high core foam densities than at low densities. However, when the blowing agent was increased from 13.7% to 16.8%, the most dramatic increase is found at lower densities. There appears to be a change in the controlling process variable, depending on whether there is a high or low core foam density at this mold temperature.

The effect of blowing agent on skin formation at two densities is described in Figure 6. Again, the mold temperature was 140°F. At 7 lb/ft^3 core foam density, the slope of the skin-versus-per cent blowing agent curve is increasing with increased per cent blowing agent. The opposite is true at 16 lb/ft^3 core density. In this case, the skin increases with increase in blowing

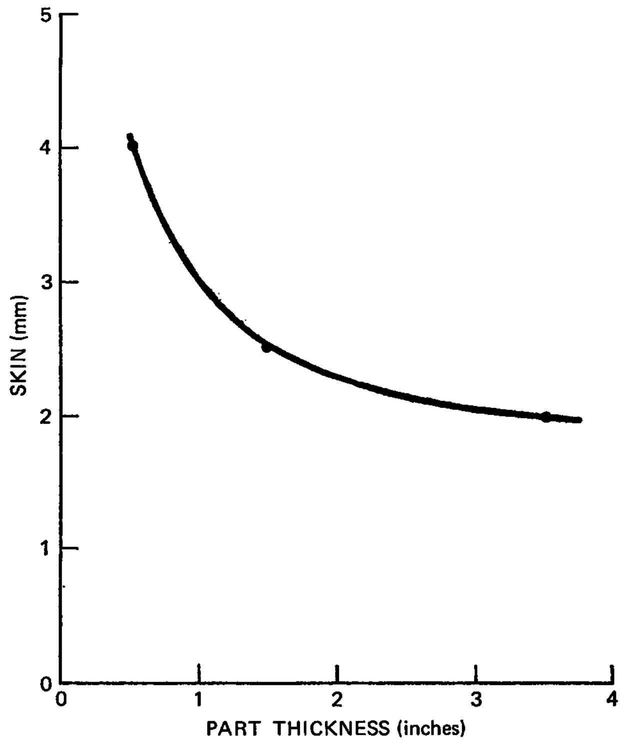


Fig. 7. Effect of part thickness on skin formation.

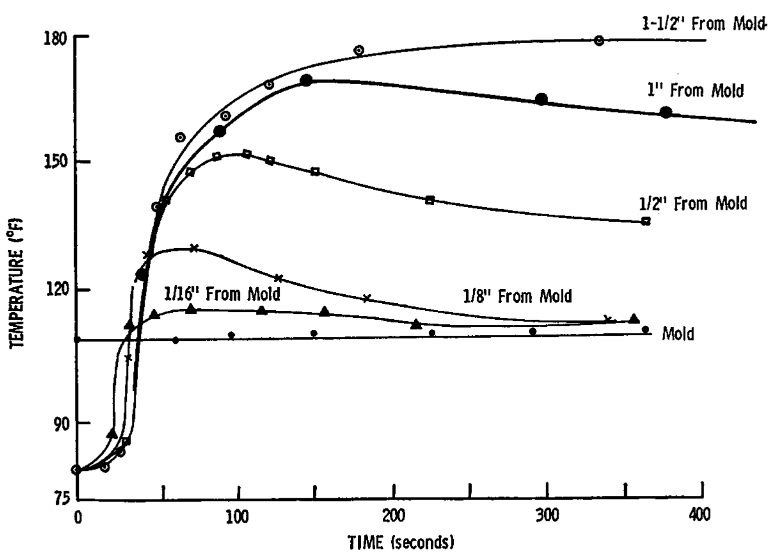
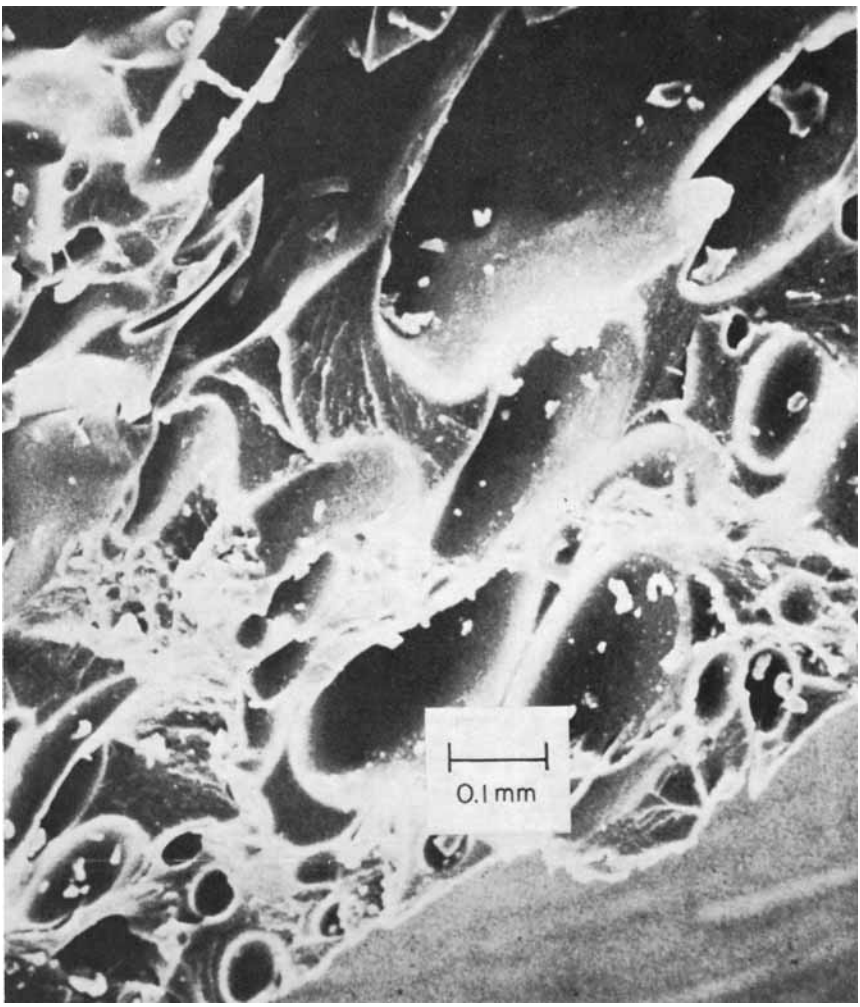


Fig. 8. Temperature profile in test mold.

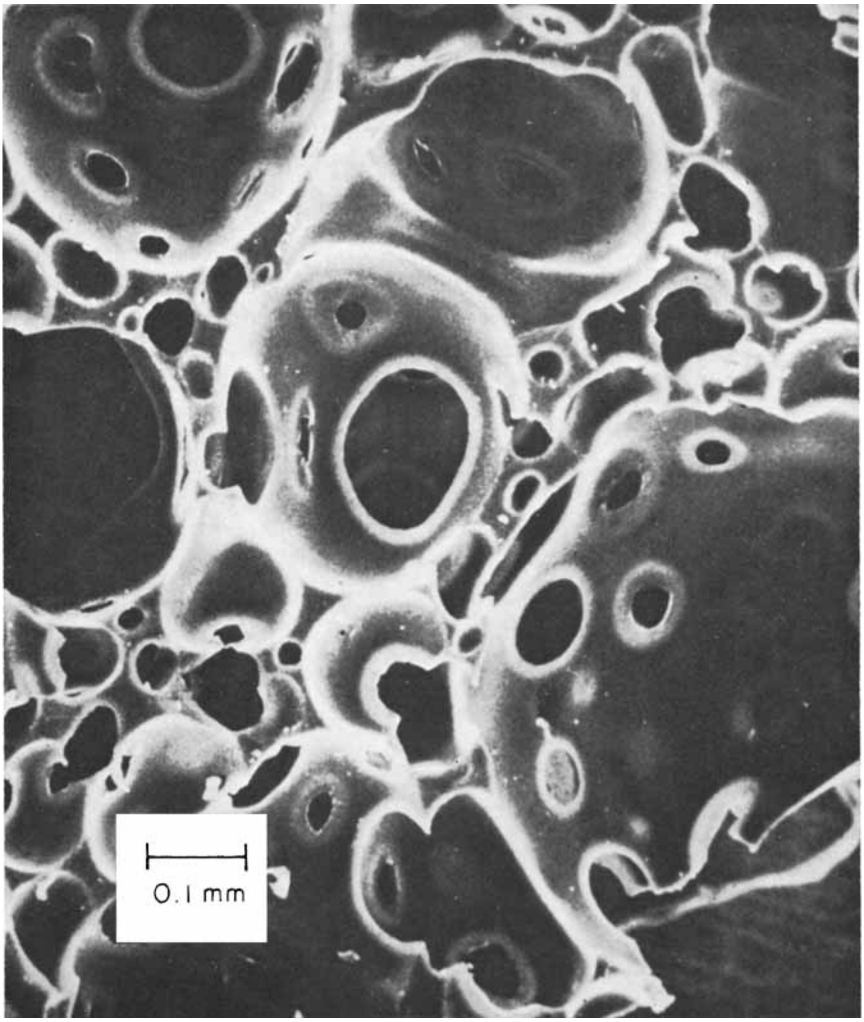
agent but at a decreasing rate. This change is indicative of a change in controlling variable.

Part Thickness. The part thickness was found to have a marked effect on skin formation, as is seen in Figure 7. This sample had an 18 lb/ft^3 core density in the widest section of the mold (Fig. 2). There was 13.7% blowing agent, and the mold temperature was maintained at 125°F. The skin was found to increase from 2.0 mm to 2.4 mm from the 3.5-in. section to the 1.5-in. section of the mold. The amount of skin increased more sharply as the mold size was reduced further, as is seen by the rapidly increasing slope of the skin formation-versus-part thickness relationship.



(a)

Fig. 9 (*continued*)



(b)

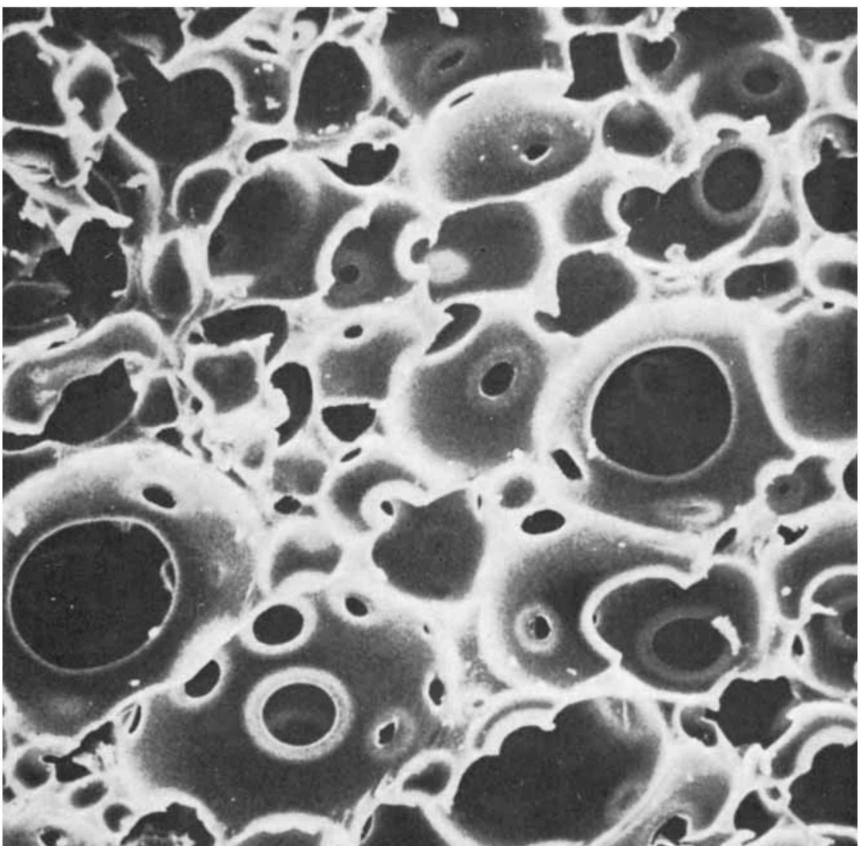
Fig. 9. Electron micrograph of free-rise foam.

Temperature Profile

Several experiments were conducted which measured the thermal profile during foaming. The results generally followed those graphed in Figure 8. In this example, the mold was maintained at 110°F, and the core foam density was measured at 9 lb/ft^3 with a free-rise foam density of 5 lb/ft^3. The temperature rose first near the mold wall. As the distance from the mold was increased, the maximum in the temperature curve generally occurred further down the time line. At $^1/_8$ in. from the mold, the maximum of 130°F was recorded at about 70 sec into the run.

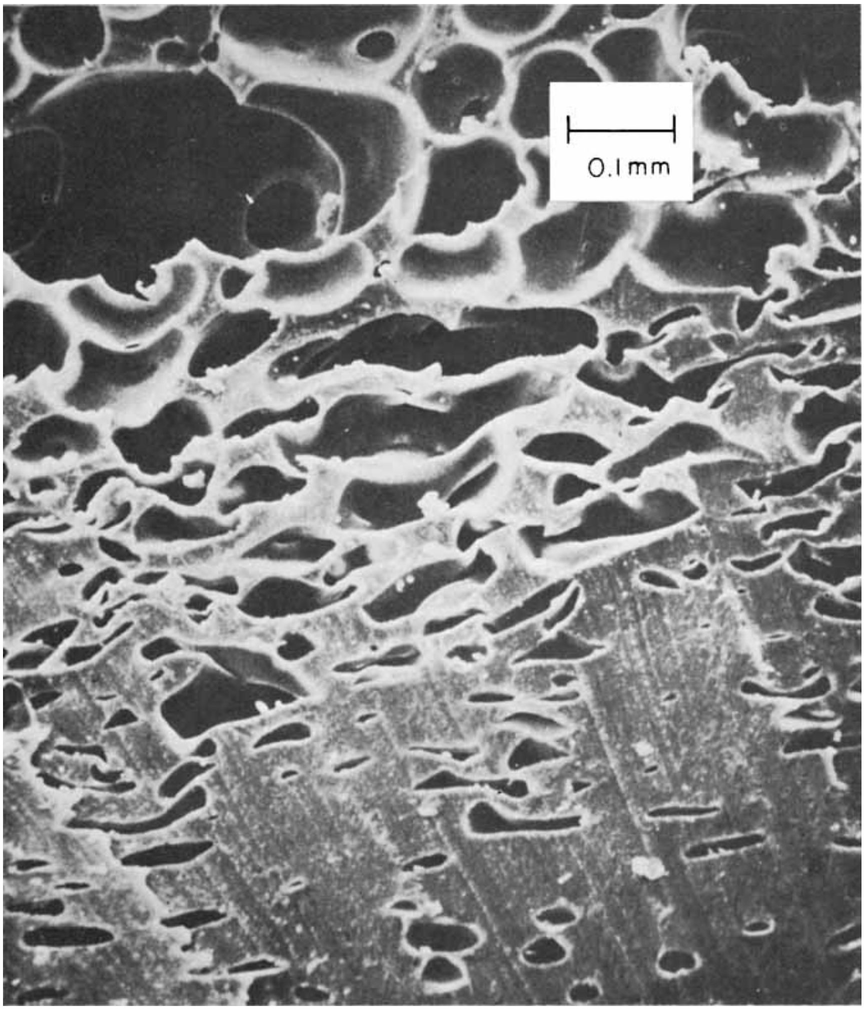
Foam Morphology

Free-Rise Foam. The morphology of the foam was examined using a scanning electron microscope. The electron micrographs in Figure 9 were taken of a sample which had been free-raised to a core foam density of 4.7 in an aluminum mold. The sample was cut perpendicular to the mold surface; thus, in effect, the pictures were taken looking down on the foam. The structure of the core foam is shown in Figure 9a. The cells are 0.2 to 0.4 mm in diameter. All of the cells appear to be open but have not drained completely. Therefore, the classical hexagonal strut relationship is not obvious. The mold foam interface is shown in Figure 9b for the free-rise foam. The lower right-hand corner of the electron micrograph shows the extent of skin formation by the free-rise foam. The skin is less than 0.1



(a)

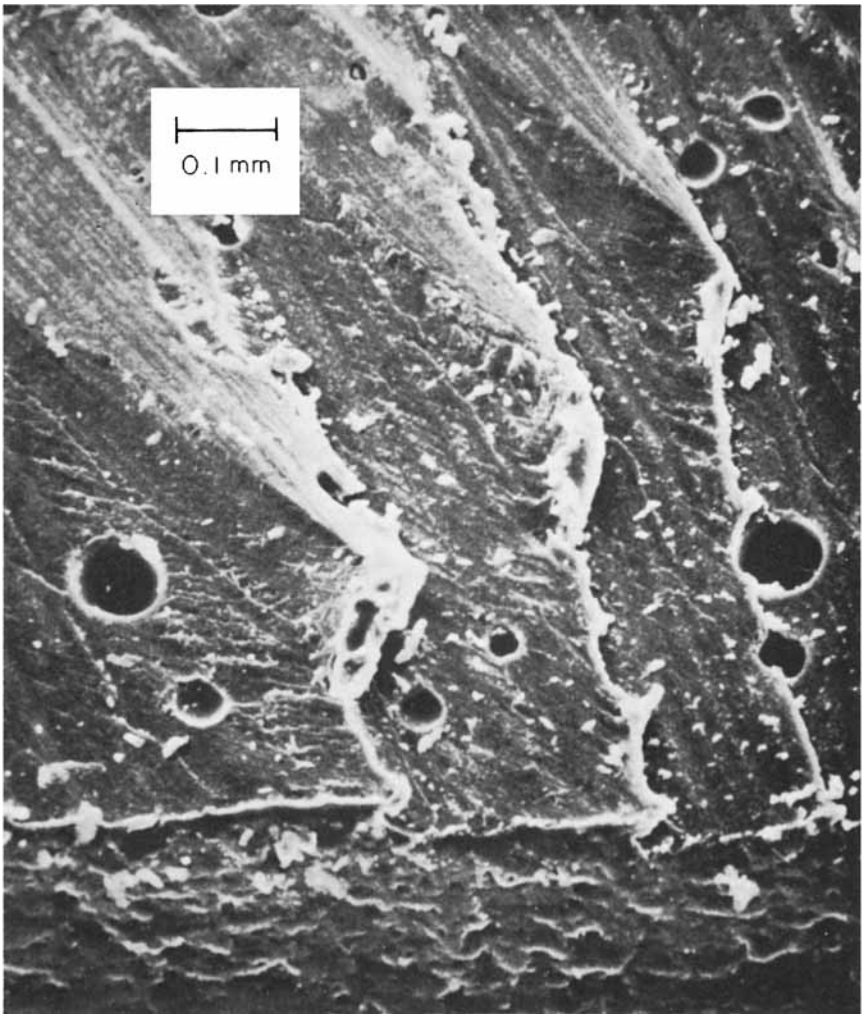
Fig. 10 (*continued*)



(b)
Fig. 10 (*continued*)

mm thick and contains numerous pinholes. The large cells of the core foam extend to within 0.1 mm of the foam mold boundary. In practical terms, this means no skin was formed.

Packed Foam. The morphology of the packed foam is depicted in Figure 10. Figure 10a is typical of the packed core foam samples. The cell structure is similar to the free-rise foam in Figure 9a, except that the cell size is now reduced to 0.1–0.2 mm in diameter. Again, the cells have not completely drained. In Figure 10b, the transition region between the core foam at the top and the skin at the bottom is pictured. The skin is mostly solid urethane with random cells. In many instances, the small random cells appear to be coalescing in this transition region. At the transition, the cell are flattened, suggesting that they were moving in the direction of the mold wall when gelation occurred. The transition region is, at most, 0.2 mm



(c)

Fig. 10. Electron micrograph of integral-skin foam.

thick. The elongated cells appear to become round as one moves away from the transition region further into the skin. This indicates that the skin area was a liquid which allowed the fluorocarbon to equilibrate to the most stable shape, a sphere, before the skin gelled. Figure 10c is the skin area. Here we see the random cells which are somewhat larger than those near the transition region. The mold–foam interface is at the bottom of the picture, and the light ridges are the result of the razor blade cuts during sample preparation. It was observed that the random cells in the skin area comprised about 10% of the total area. In all samples, the skin was not cell free, but it had random cells which, in this system, were always about the same size. This indicates that the liquid drops which made up these cells were stable at the surfactant level of this foam.

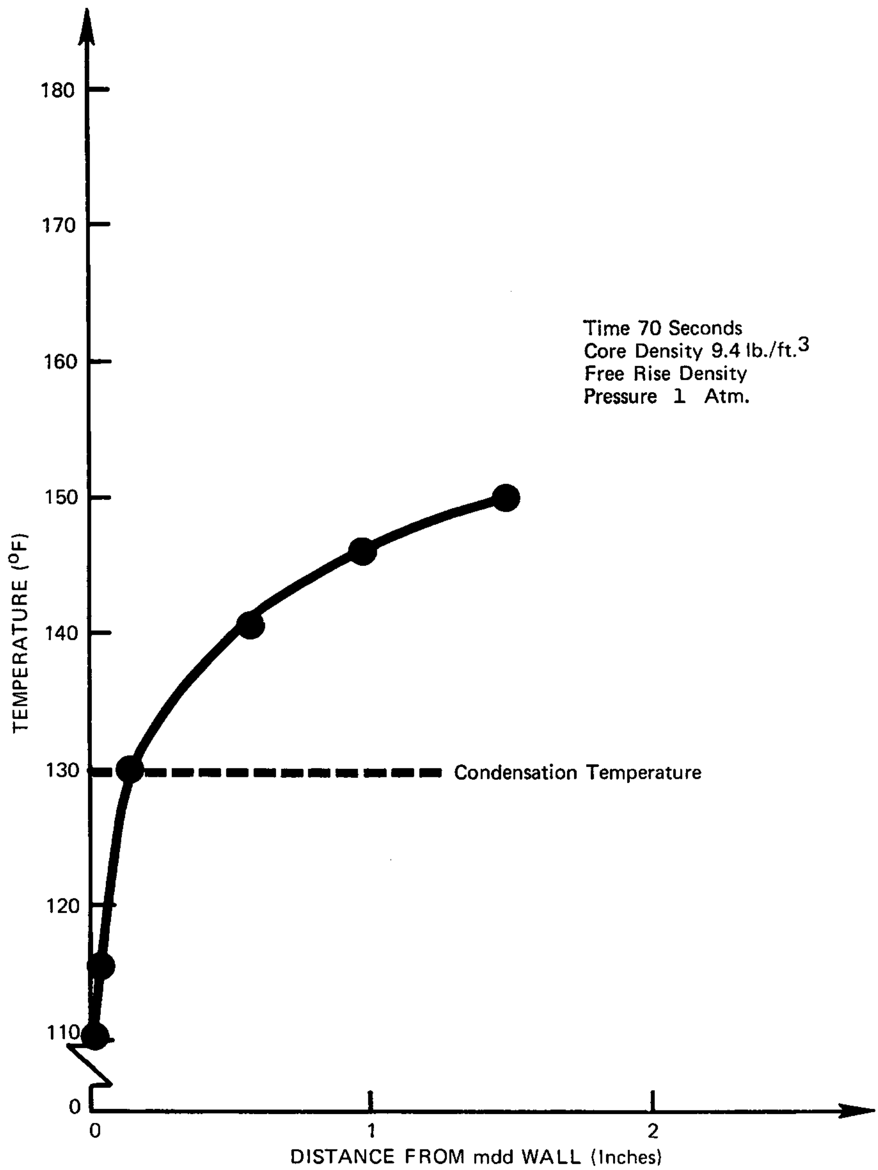


Fig. 11. Intersection of condensation temperature and temperature gradient.

Skin-Forming Mechanism

Drawing from the preceding discussion, the following skin-forming mechanism is proposed for fluorocarbon-blown systems. After the foamable mass is charged in the mold, the foam blows first near the mold. This is a result of the mold being at a temperature above the normal boiling point of the blowing agent. Also, the reaction rate near the wall would initially be more rapid because heat is being conducted from the wall to the foaming mass. This hypothesis is borne out by the temperature profile data.

At the time when the foam temperature near the wall is equal to or greater than the mold, the heat conduction process is reversed and the mold removes heat from the foaming mass. With the mold filled and under a packed condition, the pressure in the mold rises owing to the continued evaporation of fluorocarbon and the increase in average bulk temperature. The increased pressure causes the condensation temperature of the blowing agent to increase according to the relationship

$$TC = TB + 83.3 \ln P$$

where TC is condensation temperature, °F; TB is normal boiling point, °F; and P is pressure, in atmospheres. For most fluorocarbons, the constant is 83.3°F.

The interaction of the temperature gradient from the bulk foam to the mold wall and the changing condensation temperature cause skin to form. The blowing agent will condense to a liquid at all points where the foam temperature is less than the condensation temperature, which is associated with the mold pressure. This condensation continues until the foam system gels. Figure 11 shows the intersection of the condensation temperature and temperature gradient for the foam used to obtain the data in Figure 8. This system had a gel time of 70 sec, and the pressure was calculated from the ratio of free-rise density to core foam density of the packed system. The condensation temperature was calculated using the normal boiling point of the lower boiling fluorocarbon since the cells would not collapse until it had condensed. The skin-forming mechanism in integral-skin foam process is, therefore, thought to be a dynamic process which involves the condensation of the blowing agent due to increased boiling point. The blowing agent condenses into the foam mass up to a point where the temperature, owing to the heat loss to the wall, equals the condensation temperature of the blowing agent.

It can be shown that the pressure in a packed system is proportional to the ratio of core foam density to free-rise density. Using this fact with the proposed mechanism, the data presented in Figure 5 can now be consistently explained. At low densities, increasing the amount of blowing agent accounts for more of the pressure change than does the increased core foam density over that of free rise. However, at high densities, it is the pressure generated by the packing which accounts for the majority of the pressure change. Therefore, increasing the blowing agent from 11.8% to 16.8% has a greater effect on skin formation at low density but a much smaller effect at high density.

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