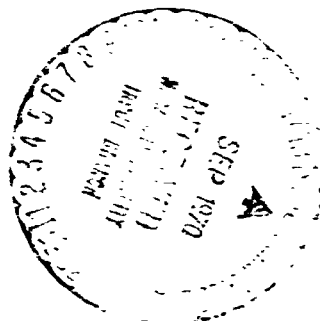**NASA TECHNICAL**
MEMORANDUM

REPORT NO. 53917

A MICROSCOPIC STUDY OF SOLID/LIQUID PHASE CHANGE IN SEVERAL MEMBERS OF THE PARAFFIN FAMILY

By Barbara E. Richard and Tommy C. Bannister
Space Sciences Laboratory

September 16, 1969

NASA

George C. Marshall Space Flight Center

Marshall Space Flight Center, Alabama

N70-37509

(ACCESSION NUMBER)		(THRU)
25		
(PAGES)		/
53917		(CODE)
(NASA CR OR TMX OR AD NUMBER)		18
		(CATEGORY)

FACILITY FORM 602

MSFC - Form 11 m (September 1968)

IN-SSL-T-68-9

Changed to TM X-53917, September 16, 1969

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Barbara E. Richard
and
Tommy C. Bannister

George C. Marshall Space Flight Center
Huntsville, Alabama

ABSTRACT

This report presents the findings of a preliminary study in which time-lapse movies were taken through a microscope to investigate the solid/liquid interface during phase change. The apparatus, procedure, materials used, and results are discussed. Recommendations are made for improvements in technique and equipment.

The interface morphology varied greatly during freezing with different materials. All sample materials except water showed microscopic peaks along the interface, but these peak heights varied from a maximum of 0.17 mm for tetradecane to a maximum of 2.25 mm for a binary mixture of 5 percent hexadecane in octadecane.

The feasibility of using this technique to study the effects of convection, bubble formation, freezing and melting rates, and other parameters is shown.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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A MICROSCOPIC STUDY OF SOLID/LIQUID PHASE CHANGE IN SEVERAL MEMBERS OF THE PARAFFIN FAMILY

INTRODUCTION

The processes involved in solid/liquid phase change have been subjects of interest to scientists of several different disciplines for years. In metallurgy, semiconductors, biochemistry, and other related fields, a more complete knowledge of the mechanisms of crystal growth would prove invaluable. Using the latent heat of fusion, which is inherent in the freezing and melting of a substance, presents an attractive method of thermal control in spacecraft [1,2]. Yet without a thorough understanding of the processes of solidification, liquefaction, and nucleation, there are reservations about using this method under space conditions. Using phase change materials in conjunction with presently used systems (coatings, louvers, heat pipes, and others) presents a means of increasing dependability, lifetime, and adaptability.

This method has led to a series of supporting scientific studies, one of which this report covers. Using heats of fusion is feasible, but at present without further investigation the mechanisms involved in the processes of melting and freezing are not understood well enough to proceed with phase change as a thermal control system. For instance, how does the role of convection affect phase change? Will the absence of convection in 0-g lead to unknown difficulties? How does the presence of bubbles and voids affect the system? And in space, what will the differences in these effects be? These and other questions concerning nucleation, the effects of thermal cycling, freezing and melting rates, and other parameters are of vital interest to scientists in many fields.

The technique for microscopic studies of solid/liquid phase change was developed by L. J. Thomas and J. W. Westwater of the University of Illinois in 1963 [3,4]. Their subject materials included n-octadecane ($C_{18}H_{38}$), n-hexadecane ($C_{16}H_{34}$), and binary mixtures of these two paraffins. The study presented in this report is of an exploratory nature aimed at further development of the microscopic technique of crystal growth studies. Development of this technique was necessary before the initiation of further studies. Quantitative studies are now under way.

The paraffins provide excellent material for studies of crystal growth by microscopic observation. They are straight-chained hydrocarbons with relatively high heats of fusion; their melting points, varying as a function of number of carbons in the chain, cover a wide range of temperatures. The major advantage in using the paraffins is that in the liquid state and as single crystals they are transparent, and in the solid bulk they are translucent. This fact makes microscopic observation of the freezing/melting interface possible and this is not feasible for metals or other opaque substances. One must resort to such methods as decanting the opaque liquid (thus interrupting the process) to study crystallization in metals. By using a transparent liquid, the process can be observed as it occurs.

The basic theory of solidification, liquefaction, nucleation, and related heat transfer problems is discussed at great lengths by many authors, including those in References 3, 5, and 6. Two primary factors in this study are the latent heat of fusion and convective currents.

When a solid melts, the amount of heat which must be added at its melting point to cause the molecules to become sufficiently detached from each other to be termed a liquid (still at its melting point) is called heat of fusion.

A research study [6] conducted by Lockheed Aircraft Corporation for NASA has shown that convection also plays a dominant role in phase change. Three types of convection are of prime importance: Rayleigh convection, R (influenced by gravity), Marangoni convection, B (not influenced by gravity), and inertial convection (caused by volume changes between solid and liquid). Convection in some form is almost a necessity in solidification (the molecules in the liquid must move to available lattice sites) and in liquefaction (the molecules in the solid must move into the melt). In a gravity field both the Rayleigh number and the Marangoni number play roles in convection. In the absence of a gravity field, Rayleigh convection would not occur; however, it is still possible for convection of the Marangoni type to occur. At present, it is uncertain how much of the convection observed on earth is the result of the inertial and Marangoni types. (The influence of each type upon the total amount of convection seen is also unknown.)

Further scientific research in the area of convective effects on solidification and liquefaction as well as the effects of space conditions on convection, would add much to the growth theories. Direct microscopic observation of the advancing interface can be used quantitatively to measure velocity and velocity distribution throughout the bulk, define interfacial geometry as a function of growth rates, determine growth rate as a function of thermal gradients, define

mechanisms of heat transfer, determine the effect of bubble and void formation on solidification, determine possible effects of magnetic fields, and evaluate many other aspects of crystallization.

Mathematical equations defining boundary conditions and giving analytical solutions to problems of heat transfer have been formulated. These solutions involve assumptions such as materials of infinite thickness that can be verified or rejected through the microscopic studies. Realistic laboratory conditions do not always allow these analytical solutions. Much work has been done to develop solutions which approximate boundary conditions.

One such model of the freezing and melting process is given by Chalmers [5]. His model gives the rates of melting and freezing as follows:

$$R_m = N_s A_m G_m \nu_s \exp(-Q_m/RT)$$

$$R_f = N_l A_f G_f \nu_l \exp(-Q_f/RT) \ ,$$

where R_m and R_f are the rates of melting and freezing; N_s and N_l are the number of atoms per unit area at the interface in the solid and liquid; A_m and A_f are accommodation factors which determine the probability that the atoms of one phase can be geometrically accommodated in the other phase; G_f and G_m are the proportion of atoms in one phase which have all vector factors required for the atoms to leave that phase; ν_s and ν_l are the vibration frequencies for atoms in the solid and the liquid so that $\nu_s \exp(-Q_m/RT)$ and $\nu_l \exp(-Q_f/RT)$ are the number of times per second an atom at the interface has the energy required to be in the other phase. At the equilibrium temperature (T_E), $R_m = R_f$, these two processes are assumed to occur simultaneously and independently with their relative rates depending on temperature as shown in Figure 1.

The geometrical terms in this model (A and G) are rather vague. It is in these terms that convection enters by changing the position of atoms in the liquid. How convection affects these terms is not known at present.

In other models, as in this case, the effects of convection and gravity have virtually been ignored. One reason for ignoring the role of convection is that the interface kinetics involved in phase change are not completely understood.
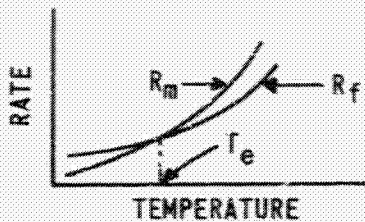
APPARATUS AND PROCEDURE

FIGURE 1. DEPENDENCE OF MELTING AND FREEZING RATES ON TEMPERATURE

A photograph of the test apparatus is shown in Figure 2. Note that the camera, microscope, light source, and test cell are all securely mounted on a steel base plate to minimize vibration effects on the film. A schematic of the entire apparatus is shown in Figure 3. Figure 4 illustrates some features of the test cell. The inside dimensions of the test cell were 1 1/4 x 1/2 x 1/2 inches. The walls of the cell were made of 1/16-inch Plexiglas for all runs except those in which a binary mixture of 25 percent hexadecane and 75 percent octadecane was photographed. In these runs 3/64-inch vinylite was used.
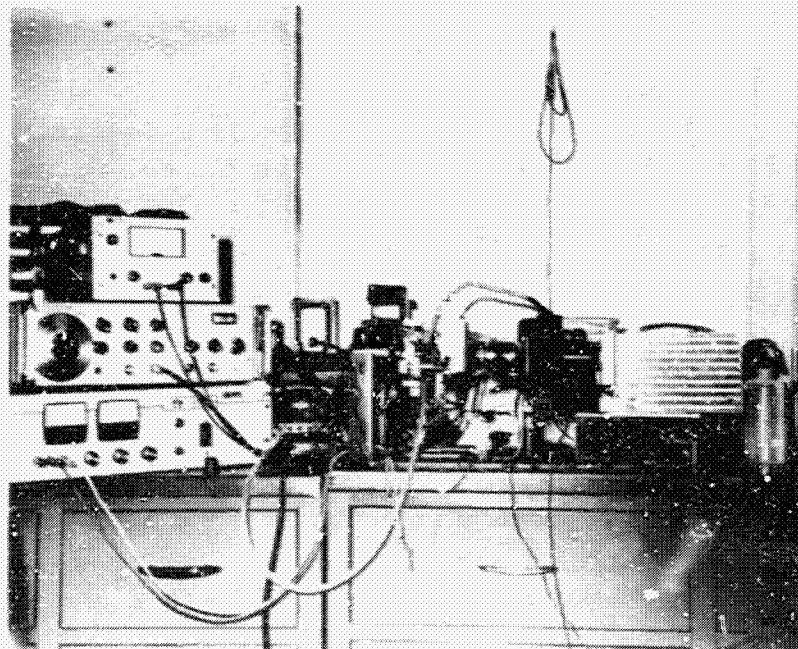

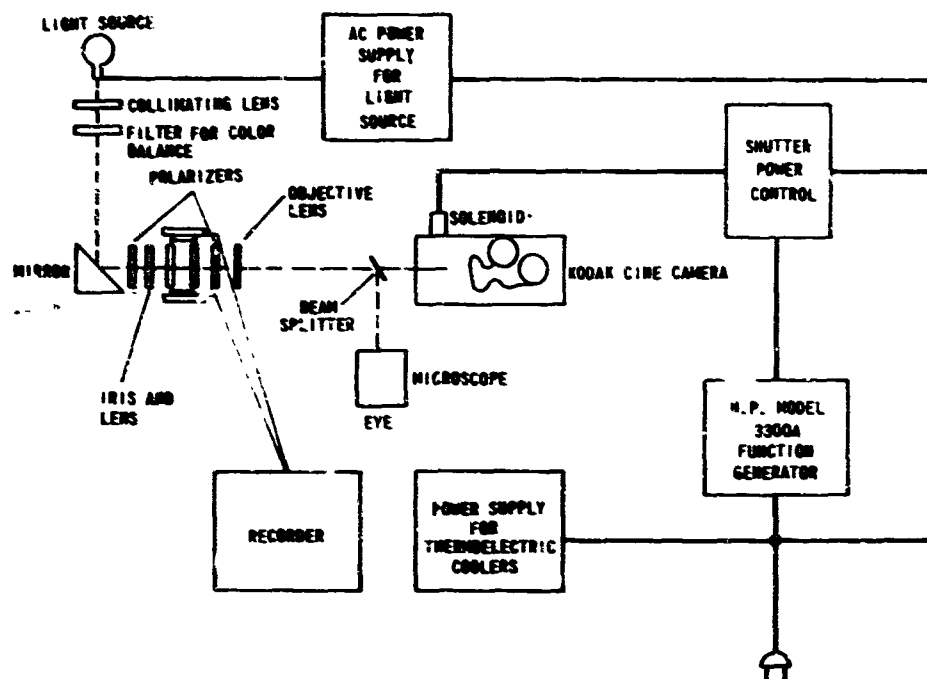FIGURE 2. IN-HOUSE TEST APPARATUS
(PHOTOGRAPH)

FIGURE 3. SCHEMATIC OF IN-HOUSE TEST APPARATUS

A Peltier device was placed at each end of the cell to heat and cool the ends independently. Thus the sample material could be melted or frozen vertically either upwards or downwards. Aluminum blocks were used between the Peltiers and the test cell to assure an even distribution of heat. Brass heat sinks required to dissipate waste heat from the Peltiers were made, and pipes through which tap water was circulated (Fig. 5) were machined inside. Two thermocouples constructed from 0.025-inch diameter copper-constantan wires were placed on the aluminum blocks next to the cell itself so that the temperature recorded on the Speedomax W recorder was approximately the actual temperature of the interface between the aluminum and the test material. The temperature of the top and bottom thermocouples was recorded alternately every two seconds. As the melting point of the sample materials (except octacosane) was near room temperature, extraneous lateral heat flow through the cell walls was ignored in these studies.

Volume change was compensated for by a small vent reservoir in the top aluminum block slanting down to the inside of the test cell. The reservoir worked very well when freezing from the bottom because the liquid was pushed upward through the vent. When freezing from the top, however, the vent was closed by the solid, and there was no room for expansion. In these cases the
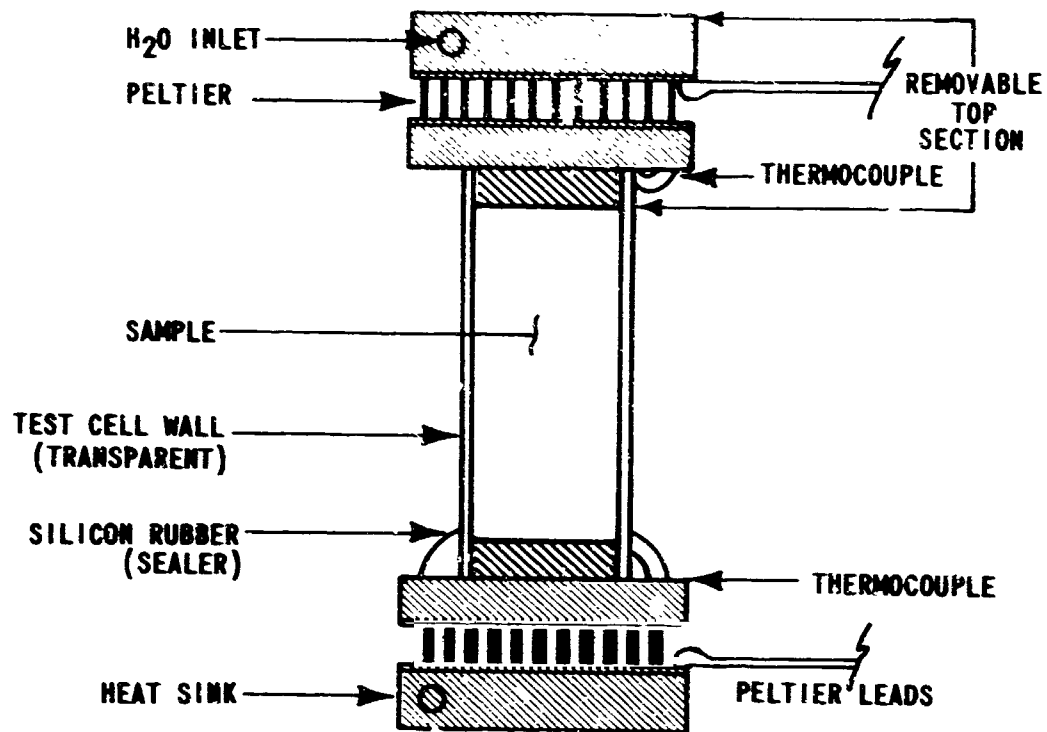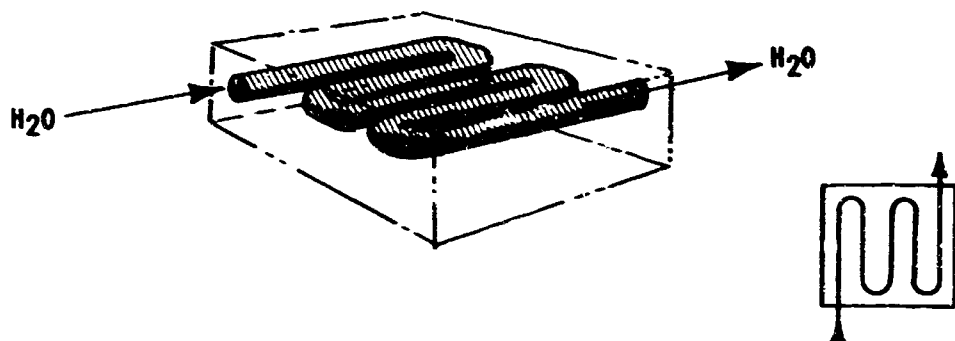
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FIGURE 4. SCHEMATIC OF TEST CELL

FIGURE 5. HEAT SINK

amount of pressure buildup inside the test cell was unknown, and such runs were watched closely. Several factors lead to the conclusion that pressure buildup does not affect cell performance or crystal growth patterns. The sample materials are slightly compressible; the test cell is slightly flexible; and no observed differences were found in the solidification of the sample materials at various temperatures.

Also from the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T(V - V_s)} \quad ,$$

(where dP/dT is the change in pressure with a change in temperature; ΔH_{fus} is the heat of fusion in liter-atmospheres; T is the melting point in °K; and $V - V_s$ is the volume change from liquid to solid), it has been found that a change of 1° in the melting point of water requires a pressure of 133 atmospheres. In other words, an increase in pressure of one atmosphere lowers the melting point by 0.0075° [8].

Sample materials included n-octacosane ($C_{28}H_{58}$), n-eicosane ($C_{20}H_{42}$), n-octadecane ($C_{18}H_{38}$), n-hexadecane ($C_{16}H_{34}$), n-tetradecane ($C_{14}H_{30}$), water, and binary mixtures of 5 percent hexadecane in octadecane and 25 percent hexadecane in octadecane. All samples except water exhibited polycrystalline material and single crystal spikes at the operating magnification.

Melting points from the literature are given in the following table:

Material	Melting Point – °C
H_2O	0
Tetradecane	5.5
Hexadecane	20
Octadecane	28
Eicosane	38
Octacosane	61

The laboratory setup was constructed around a Letz microscope with a beam-splitting prism situated in the light path of the tube. The light beam was split in a ratio of 80:20, with 80 percent passing through the phototube and 20 percent through the observation eyepiece tube. The light source was a 6-V, 30-W filament bulb mounted in a universal lamp housing. Since the shutter speed on the 16-mm Kodak Cine movie camera was fixed at 1/50 sec, the exposure was controlled by the light intensity or the aperature diaphragm or both. With black and white film, exposure was controlled chiefly by the light intensity. The filament temperature recommended by the film manufacturer for proper color balance in the use of color film was 3200°K so that the aperture diaphragm was the chief means of controlling the exposure.

Although large magnifications were desirable, there was a point beyond which the shorter focal lengths of the higher powered objective lenses proved useless with the apparatus used. The thickness of the sample cell made focusing on the interface in the bulk impossible at the higher magnifications.

Two objective lenses were used. One produced a magnification of 5X on the film, whereas the other gave a magnification of 17.85X. The short focal length of the higher power objective made focusing with this lens a problem. For example, it was only possible to focus just inside the wall, thus creating the possibility of the runs being affected by heat transfer through the wall. Pictures taken with the lower magnification lens were focused in the bulk, thus eliminating most boundary effects. One of the major advantages of using a transparent liquid and a translucent solid is the ability to study growth in the bulk, and this possibility was utilized best by using the lower magnification objective lens. Fortunately this magnification was sufficient to show the interfacial features of the sample materials used. This lens had a field of view 3 mm x 2 mm.

Most runs were taken at a framing rate of 2.0 frames/sec. The framing rate was controlled by a Hewlett Packard function generator, Model 3300A. This furnished a timing pulse to a silicon control rectifier circuit. The power from the SCR circuit operated an electromechanical solenoid which actuated the shutter (Fig. 3). After a warmup period of 30 to 45 minutes, the pulses from the function generator were compared with the timing signals from WWV, and there was no significant discrepancy.

The test cell was filled by removing the top section (Fig. 4) and pouring in the sample material. With the top replaced, the test cell was placed in a special mount attached to the microscope. Before filling the cell, each sample was filtered to remove impurities, and the cell was thoroughly cleaned by boiling in an Alconox/water solution three times for fifteen minutes each time. The cell was then rinsed thoroughly in distilled water.

The mount which held the test cell could be traversed both vertically and horizontally maintaining the solid/liquid interface in the field of view.

Since the sample materials were colorless, black and white film was first used. Three types of film were tried: Tri-X reversal, Plus-X reversal, and infrared. Plus-X reversal gave the best images. Runs from all three types of film were assembled in Reel 1.

The use of polarized light with colored film resulted in movies which gave more depth perception than the black and white. Several runs were made using colored film and were assembled in a separate movie (Reel 2). Sample materials for the colored film were water and binary mixtures 5 percent hexadecane in octadecane and 25 percent hexadecane in octadecane. A color-compensating filter was required when color film was used. Normally an Ortholux WXYEE blue filter was placed in the light beam. This filter produced a reasonable color balance. The polarizers were placed in the light beam before and after the sample materials (Fig. 3). When observed under these conditions, the crystals were multicolored because of birefringent properties. As a crystal thickens, the color changes. Thus an idea of the rate at which a crystal's thickness changes can be obtained. It is feasible that this technique can be developed into a method of measuring growth velocities with respect to crystal thickness.

Organic materials tend to dissolve gases readily. These gases were released as bubbles in the melting and freezing processes. No attempt was made to remove these dissolved gases. In several cases (notably water) the bubbles could be seen redissolving on melting if they did not become large enough to rise to the top of the cell by buoyancy forces. Octacosane was particularly difficult to photograph because of the very large bubbles (sometimes as large as 2mm in diameter) which formed when the material was frozen. The cell was vibrated to release these bubbles so that the advancing interface could be photographed. This procedure could not be continued for any length of time because a void was produced by the rising bubbles between the liquid and the upper heat source. It was almost impossible to photograph

octacosane freezing from the top since the bubbles completely covered the interface, thus cutting off the solid entirely from the liquid. By using a steady flow of hot air, however, to melt a "reservoir" in the solid to absorb the bubbles, pictures were obtained of octacosane melting from the top. In these cases the hot air was directed toward the back side of the test cell until sufficient solid was melted to accommodate the bubbles formed during freezing. The solid was allowed to come to equilibrium with the liquid, the substance was melted, and the photographs were made.

Bubbles were seen under both freezing and melting conditions in all the samples, but were fewest in the two binary mixtures. Water was an interesting sample. No crystalline structure of water could be seen at the stated magnification. The size of the bubbles which formed at the interface during freezing remained approximately constant in the liquid for awhile but left a trail (a long cylindrical void) in the solid as the interface advanced. An explanation of this type of bubble formation is given by Chalmers [5].

Velocity measurements were obtained by defining the time period required for the solid/liquid interface to traverse the field of view. The maximum velocity was recorded on the film for each run.

In the runs with "snow" (observed in the binary mixture 5 percent hexadecane in octadecane when there was solid, on both top and bottom), the growth velocity of the interface was not measured. As a matter of interest, however, the velocity of crystals falling or moving in convective currents was measured. This is an indication of the amount of convection obtained with very small thermal gradients. After each 32 frames the velocity of five crystals was measured and averaged. Then the maximum average value for the run was given as the "Maximum Velocity."

Temperature profiles were taken directly from the recorder. One problem encountered with the recorder used concerned the fixed temperature span and a fixed zero position. In the process of freezing or melting, the thermocouple leads to the recorder had to be reversed. This was impractable during runs. In several cases the temperatures went off-scale.

RESULTS

General

Alth ough this study was of an exploratory nature and no attempt was made analyt cally to define and evaluate the parameters involved in phase change, general observations were made which in themselves may lead to more detailed studies.

Crystalline shape and size were dependent on growth velocities and, therefore, on temperature gradient since the velocity was determined by the temperature gradient. During the freezing process the larger crystals appeared at smaller temperature gradients. These larger crystals were both longer and wider than those grown at slower velocities. A correlation of velocity and peak height for the binary mixture 5 percent hexadecane in octadecane is shown in Figure 6. Figure 7 shows a correlation between peak height and temperature gradient for this same mixture

The dissolved gases released as bubbles during freezing and melting affected the heat flow characteristics inside the cell in several ways. First, a bubble (void) formed in the solid acts as a barrier to heat flow. Secondly, bubbles in the liquid serve to stir the liquid and thus enhance convection.

Octacosane $(C_{28}H_{58})$

To reduce the lateral thermal gradient and prevent freezing on the walls, heaters (made from #30 nichrome wire) were positioned on the front and back sides of the test cell. Octacosane has a melting point well above room temperature. The interface observed in the bulk of the sample material showed peaks and valleys. Spikes of irregular shape were observed. The spikes disappeared on melting and the interface became smooth. The maximum temperature differential was 41°C with the heat sink temperature 35° to 40° below the equilibrium temperature (melting point). The longest spikes (0.5 mm long) were observed at the point of maximum growth velocity (1.21×10^{-2} mm/sec).
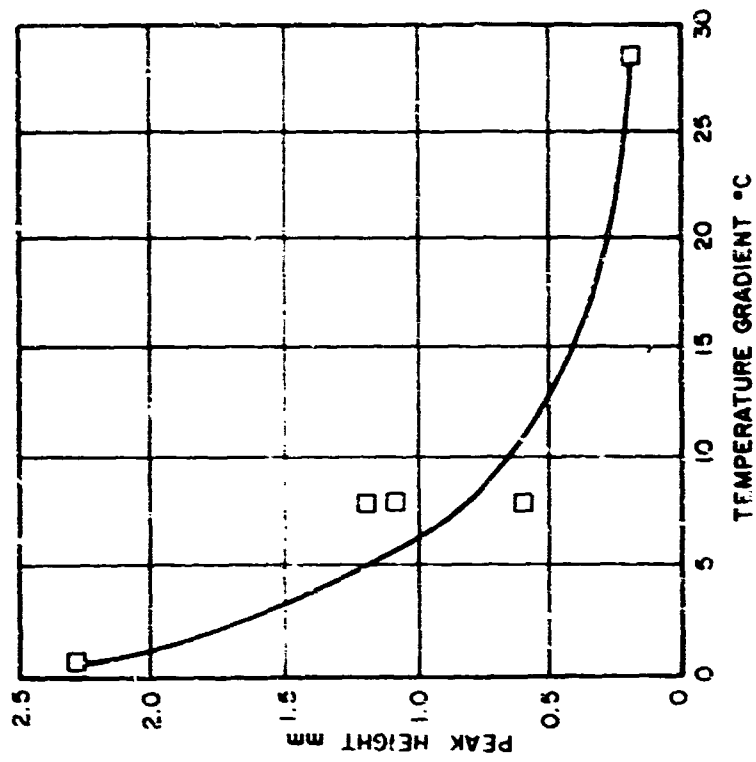
FIGURE 7. CORRELATION OF TEMPERATURE
GRADIENT AND PEAK HEIGHT IN BINARY
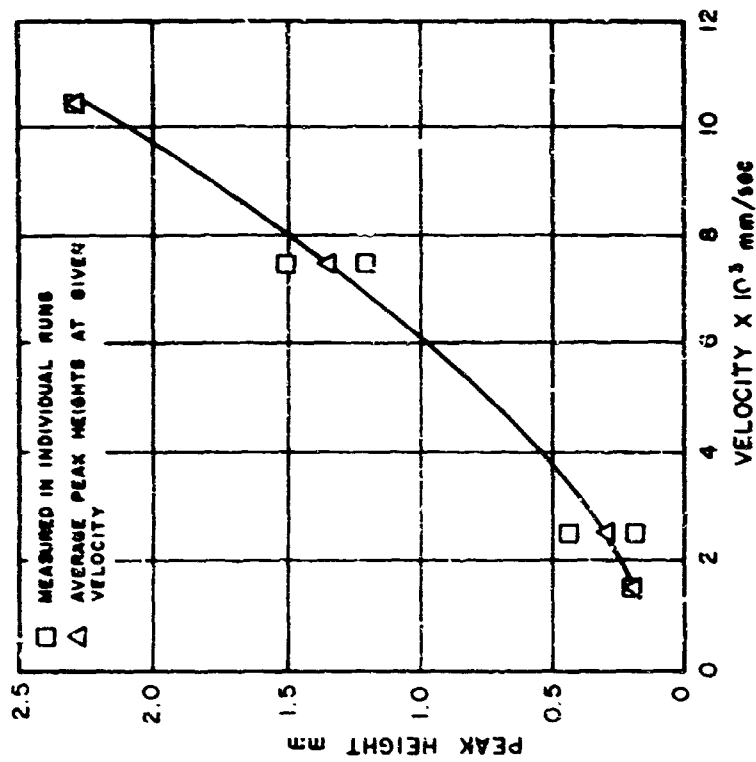MIXTURE 5 PERCENT HEXADECANE IN
OCTADECANE

FIGURE 6. CORRELATION OF GROWTH
VELOCITY AND PEAK HEIGHT IN BINARY
MIXTURE 5 PERCENT HEXADECANE IN
OCTADECANE

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Eicosane $(C_{20}H_{42})$

Although eicosane has a melting point above room temperature $(38°C)$, a stream of warm air blowing on the side of the test cell was sufficient to reduce lateral heat transfer. Pictures taken in the bulk during freezing revealed long spikes (up to 1.4 mm in length at a maximum velocity of 1.87×10^{-2} mm/sec). These spikes were similar to those present in octacosane, but they were more crowded and resembled blades of grass. When melted, these spikes disintegrate.

Tetradecane $(C_{14}H_{30})$

The melting point of tetradecane is below room temperature $(5.5°C)$; therefore dry nitrogen was circulated around the exterior of the cell to reduce water vapor condensation.

Tetradecane showed an interface which was almost smooth on freezing. Very small rounded peaks could be seen along the solid/liquid interface. When freezing the sample from the bottom, these peaks were a maximum of 0.08 mm high; when freezing from the top, the peaks reached a maximum of 0.17 mm. The variation in size of the peaks did not appear to be caused by a difference in growth velocity. The interface was smooth in all cases during melting, and myriads of small bubbles were released.

Hexadecane $(C_{16}H_{34})$

Hexadecane melts just below room temperature so was the least difficult to photograph. When solidification began, the interface was covered with many tiny spikes which grew in length and width as the interface advanced. The velocity decreased as the interface moved farther from the heat sink. At the higher velocities $(3.66 \times 10^{-2}$ to 2.0×10^{-2} mm/sec) the spikes were approximately 0.05 mm high. As the sample grew higher in the test cell and the velocity decreased (to 1.1×10^{-2}), the peaks measured were much larger $(0.75$ mm to 0.85 mm); but at slower velocities $(5.9 \times 10^{-3}$ mm/sec) the peaks were not quite so long $(0.5$ mm). As the initial spikes grew in length, their width increased at a faster rate so that the crystals appeared to become flat on top and more or less rectangular. In some cases waves were observed to form on one or another of the crystal faces. These waves were similar to ripples observed by Thomas and Westwater [3,4].

At one point, a group of spikes grew up and spread out in all directions, resembling a clump of crabgrass. This could have resulted from convective currents or some other factor.

Upon melting, the hexadecane crystals crumbled, leaving a smooth interface.

Octadecane $(C_{18}H_{38})$

Octadecane has a melting point of 28°C. When the sample was freezing, crystals of two shapes were observed: long spikes and flat crystals. These two types were not intermingled but were segregated. Both types grew at the same growth rate. It is possible that the long spikes were actually the flat crystals viewed perpendicularly to the flat face; but it is strange that these two orientations were segregated. Both types had waves; the spikes had lines which moved from the bottom to the top of the spike as it grew. On the flat crystals the waves moved along the top surface.

The melting interface was irregular in most cases and bubbles were released as in the other materials studied.

Five Percent Hexadecane in Octadecane

The melting point of this mixture is 27.3°C. During freezing the interface was very irregular: spikes grew out almost horizontally both from right to left and left to right, ahead of the bulk interface. At low growth velocities $(1.47 \times 10^{-2}$ mm/sec) these spikes were small (0.2 mm) and looked very much like hexadecane. At the highest velocity measured $(1.04 \times 10^{-2}$ mm/sec) these spikes were as long as 2.25 mm. Convective currents could be seen in several runs. These currents were especially noticeable during melting, but they could also be seen during freezing. The direction of spike growth was generally in the direction of these currents. It appears that the atomic kinetics of crystallization are slow relative to the mass movement caused by the convection present in these studies. Thus the face of the crystal which was most affected by convection (the upper face) grew slower than the underface since molecules in the liquid were moving too rapidly to become oriented properly as a new layer in the solid. The result of this condition was that the crystal spikes grew in an almost horizontal direction; adding molecules to the underface more rapidly than to the upper face. This type of growth is illustrated in Figure 8. These larger crystals were observed, as previously stated, at
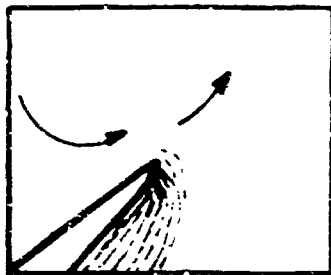
12

FIGURE 8. SPIKE GROWTH IN
BINARY MIXTURE 5 PERCENT
HEXADECANE IN OCTADECANE

higher velocities — that is to say, at lower temperature gradients. During melting, bubbles which had been trapped in the solid were released. The interface was relatively smooth after the initial layer of single crystals melted. Attempts to observe the very large peaks ("castles") of solid (as high as 0.01 in.) reported by Thomas and Westwater [3,4] were unsuccessful. In some melting runs, however, amorphous-looking material was observed intermingled with crystalline material. Apparently these amorphous volumes were the result of a separation of components, the same as was the case with the large peaks discussed by Thomas and Westwater.

Another striking phenomenon observed in the binary mixture of 5 percent hexadecane in octadecane occurred when solid had been allowed to form at both the top and bottom of the test cell: Individual crystals were observed to fall from the top into the liquid, and when large amounts of convection were present, individual crystals were swept up in these currents from the bottom into the liquid. Because the velocities were much faster, the framing rate was increased, generally to 8 frames/sec, during these runs. These snowstorms provided an opportunity to study individual crystals. The individual crystals falling from the top were much larger than those swept from the bottom. The convection necessary to carry crystals up into the liquid is indicative of the fact that in these cases the thermal gradient in the liquid was large. In the cases where large crystals fell from the top, there was little or no convection observed. This fact coupled with the fact that the individual crystals did not appear to change in size indicates that the temperature of the liquid was uniform throughout the system. Individual crystals seen in these snowstorms had varying shapes from small squares and rectangles (as small as 0.01 mm) in some runs to large needle-like and cigar-shaped crystals (as long as 1.05 mm) in others. The average size of the crystals was about 0.4 mm. The temperature in the liquid must be almost at the equilibrium temperature since no growth or melting of the crystals was observed as they moved through the liquid. In some runs the crystals seemed to be suspended in the liquid. This may be the result of combined forces of buoyancy, convective currents, gravity, and viscosity.

Twenty-five Percent Hexadecane in Octadecane

This mixture has a melting point of 23° to 24°C. The advancing inter-
face during freezing was irregular. As in the 5 percent hexadecane in octade-
cane mixture, there were some spikes growing at an incline. The upper face
of these spikes, however, was irregular ("ruffles" appeared on this face);
these ruffles grew to be new peaks. Other crystals were feather or leaflike;
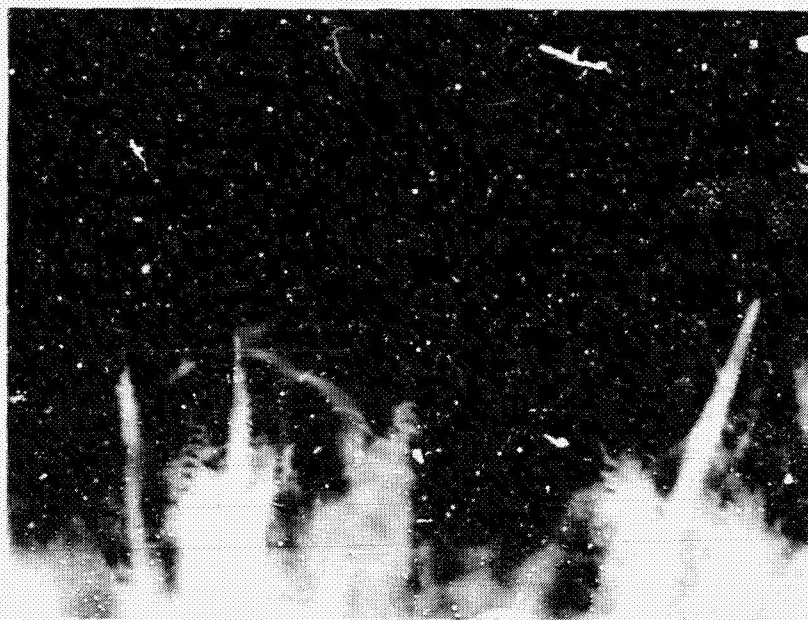these grew in concentric waves as illustrated in Figure 9.

FIGURE 9. CONCENTRIC-WAVE GROWTH PATTERN IN
BINARY MIXTURE 25 PERCENT HEXADECANE IN OCTADECANE

These leaflike crystals and spikes could be the same crystalline shape
viewed from different angles.

When freezing from the top, the crystals appeared to be more rounded
and not quite so large as when freezing from bottom (peak height, freezing
from bottom: 0.17 mm to 1.05 mm; freezing from top: 0.17 mm to 0.5 mm)
As with melting the 5 percent hexadecane in octadecane mixture, amorphous
volumes appeared among the crystalline material. This was more pronounced
in the 25 percent mixture.

Attempts to produce snow with this mixture were not so successful as with the 5 percent mixture. Only one snowstorm was recorded, and the crystal observed attached itself to the wall as it fell. These crystals were larger than those in the other mixture.

Water

Of all the test materials water was the only one in which supercooling was observed. When crystallization began, it was rapid throughout the super-cooled liquid. As ith tetradecane dry nitrogen was circulated around the outside of the cell to prevent water condensation. Bubbles were very prominent in water. Gases dissolved in the water came out of solution at the interface forming bubbles. Solid froze up around the bubbles leaving long cylindrical voids in the solid. At high velocities, as in initial growth after supercooling, the bubbles were rounder and more irregularly spaced. The slower the velocity, the larger and more regular the bubbles appeared. Bubble length varied from 0. 02 mm to 2. 0 mm and the maximum width was 0. 2 mm. When the solid melted, many of these bubbles simply disappeared as the gases dissolved in the liquid. These bubbles appeared to grow in "layers" in some cases. This could be the result of temperature gradients, pressure changes, heat flow, or some other cause.

When viewed parallel to the surface, waves could be seen along the interface. Several runs were made looking down at an angle on the interface. These runs showed lines moving around on the surface. At present, no explanation of this phenomenon exists.

In both freezing and melting runs the interface was smooth and showed no peaks.

Color Films

The films taken with polarized light and colored film had several advantages: (1) They gave better depth perception; (2) they gave an indication of crystal thickness by different colors in the crystal; and (3) they provide excellent educational material.

With the two binary mixtures a wide range of color could be seen under freezing conditions. When melting the same mixtures, however, the color range was usually less. Few colors were observed in the freezing or melting

of water samples. At the interface there was a red area which could possibly be explained as the refraction of the light through a layer of denser water or as the result of an out-of-focus crystal interface in the background, in which case there would be a greater depth of solid for the light to traverse.

CONCLUSIONS

The following conclusions are drawn from careful observation of the films made during this investigation:

1. The solid/liquid interface of the paraffins is not smooth under freezing conditions. Rather, the interface is populated by microscopic peaks, which are individual crystals growing ahead of the bulk.

2. Under melting conditions the interface appears smooth relative to the freezing interface.

3. Even when the low density material was placed at the top of the sample cell and thermal gradients were small, convection was observed as shown by the motion of dust particles in the liquid. At times this motion was more violent than would be predicted by the Rayleigh number.

4. With the binary mixture 5 percent hexadecane in octadecane, large peaks of solid extending into the liquid during melting, as reported by Thomas and Westwater, were not observed. Another phenomenon was observed with this mixture which may make possible more detailed studies of crystalline shape and size. When solid was allowed to form on both top and bottom of the sample cell, "snowstorms" of individual crystals were observed in the remaining liquid.

5. The geometry of the interface varies as the growth velocity varies. Peak heights were observed in general to be larger at higher velocities (after initial growth had taken place).

6. The growth velocity of the individual crystals at the interface often differs considerably from the average bulk growth rate.

7. All faces of the crystals do not grow at the same rate. Such anisotropic growth follows the path of least thermal resistance.

This study has shown that the technique of microscopic observation can be a valuable tool in studying the role of convection and other parameters in the processes of solidification and liquefaction. The use of Peltier devices has been shown to be effective in this application.

The feasibility of determining three-dimensional growth rates of crystals by use of their birefringent properties has been demonstrated. In the colored film colors in the crystals are caused by polarized light's entering the crystal and being refracted at different angles because of a difference in the thickness of the solid. Thus as the thickness changes with growth, the color also changes.

In several runs, notably those of octadecane and the binary mixtures, two distinct crystalline shapes were observed. In these cases a rotating test cell would be advantageous in determining whether these were actually the same crystalline shape oriented at different angles. The cell could be rotated as pictures are being taken to give a view of the same group of crystals from varying angles. Such a rotating cell is presently under development.

Another study which would prove interesting would be to remove dissolved gases from the materials in order to evaluate the effects of bubble formation.

In the studies described in this report no precautions were taken to prevent heat transfer with the room surroundings. It is desirable that heat flow be as unidirectional as possible and that more temperature readings be taken throughout the depth of the test material. Therefore, future plans include development of a double-walled cell with a vacuum between the walls and several (five to seven) thermocouple junctions inside the cell.

The value of this study lies in the fact that a capability to perform quantitative studies has been developed.

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APPROVAL

A MICROSCOPIC STUDY OF SOLID/LIQUID
PHASE CHANGE IN SEVERAL MEMBERS OF THE
PARAFFIN FAMILY

By

Barbard E. Richard
and
Tommy C. Bannister

The information in this report has been reviewed for security classifi-
cation. Review of any information concerning Department of Defense or Atomic
Energy Commission programs has been made by the MSFC Security Classifi-
cation Officer. This report, in its entirety, has been determined to be unclas-
sified.

This document has also been reviewed and approved for technical
accuracy.

G. B. Heller

G. B. HELLER
Chief, Space Thermophysics Division