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THE PREPARATION OF CAMPHOR MODELS FOR WIND-TUNNEL SUBLIMATION STUDIES; PRELIMINARY RESULTS ON THE SUBLIMATION OF A POINTED CONE

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SUMMARY

The ~~present~~ preliminary study of techniques for the preparation of camphor and naphthalene models for experimental research on sublimation cooling in hypersonic flow ~~has~~ led to the development of a vacuum sintering technique which yields uniform, homogeneous, clear and easily machinable samples. It is felt, on the basis of static and wind tunnel tests, as well as on the basis of these general observations, that models prepared in this fashion are well suited for accurate reproducible measurements of the history of subliming surfaces and that they will provide reliable data. Further tests on the physical properties of the material (such as its shear strength, its specific heat, its thermoconductivity, and so on) are under way.(1)

A method for accurate measurement of surface temperatures during the course of the destructive phase change mass transfer process is proposed and partly developed. If it proves to be totally successful, relatively complete and valuable information on the complex flow field will be obtainable with relatively simple facilities and techniques.

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The author is an Associate Professor, Department of Engineering, University of California at Los Angeles, where this experimental research was performed.

INTRODUCTION

Before a systematic experimental study of sublimation can be undertaken with reasonable ease and at reasonable cost, it would seem important to develop techniques and materials which can be tested in relatively low temperature wind tunnels. Simultaneously, a more perfect model theory should be developed, such that results of low temperature tests can be accurately interpreted in terms of prototype conditions. The test material should be well enough known so that the application of theoretical analysis can be done with reasonable certainty. This means, for one, that pure sublimation (without melting) is preferable since it is the easiest one and the simplest one to correlate with theory. It is only after a firm theoretical basis for a phenomenon is established, that semi-empirical extension to more complex phenomenon, such as boundary layer blowing by a release of high vapor pressure components of a charring material, and so on, can be considered.

There is a small number of practical chemicals which sublimate or ablate in a fashion that can be described accurately by theory, at temperatures which are low enough to make instrumentation and measurements convenient. Among them are dry ice, camphor and naphthalene.* Although these materials offer only a limited range of properties, they provide a very useful starting point for the investigation. Both camphor and naphthalene have been used in model experiments in the past, to a limited extent, (for instance, Ref. 2, 3) but it seems certain that the potential of such tests has not been fully realized.

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*Other materials considered in the literature are hexachloroethane, chloronil, ammonium chloride, and others.

The present investigation, which is aimed, in the long run, at a systematic study of phase change heat transfer on slender bodies in supersonic and hypersonic flow was initiated by a critical review of the method of fabricating models and a search for methods for measuring pertinent local quantities during the destructive tests, so as to ensure a well controlled uniform and reproducible behavior transferable to prototype materials by application of theoretical similarity laws.

Physical Properties of the Test Material

A brief summary of the basic physical constants of naphthalene and camphor is given in Table 1. A phase diagram of these substances (pure) in the low pressure region is shown in Fig. 1 and compared to some typical pressures which would exist in the wind tunnel operating from atmospheric stagnation conditions at Mach 3. The superposition of the partial equilibrium pressure governing the phase change of the material and the wind tunnel pressure does not yield a direct comparison, but it does show schematically the range of blowing parameters which can be reached. We note that in such an atmospheric stagnation pressure tunnel at Mach 3 the model surface thermodynamic conditions lie, in general, in the pure sublimation region (that is, below the solid vapor transition) except for very high blowing parameters (a blowing parameter is proportional to the ratio of the partial pressure of the subliming material to the static pressure in the wind tunnel). There is a difference of one order of magnitude in the pressure at the triple point between naphthalene and camphor. In any case, the manipulation of the stagnation pressure between one atmosphere and approximately half an atmosphere along with a manipulation of the stagnation temperature within a range not exceeding 200°C, will permit a very complete study of both sublimation and also, partially, ablation melting at Mach numbers of

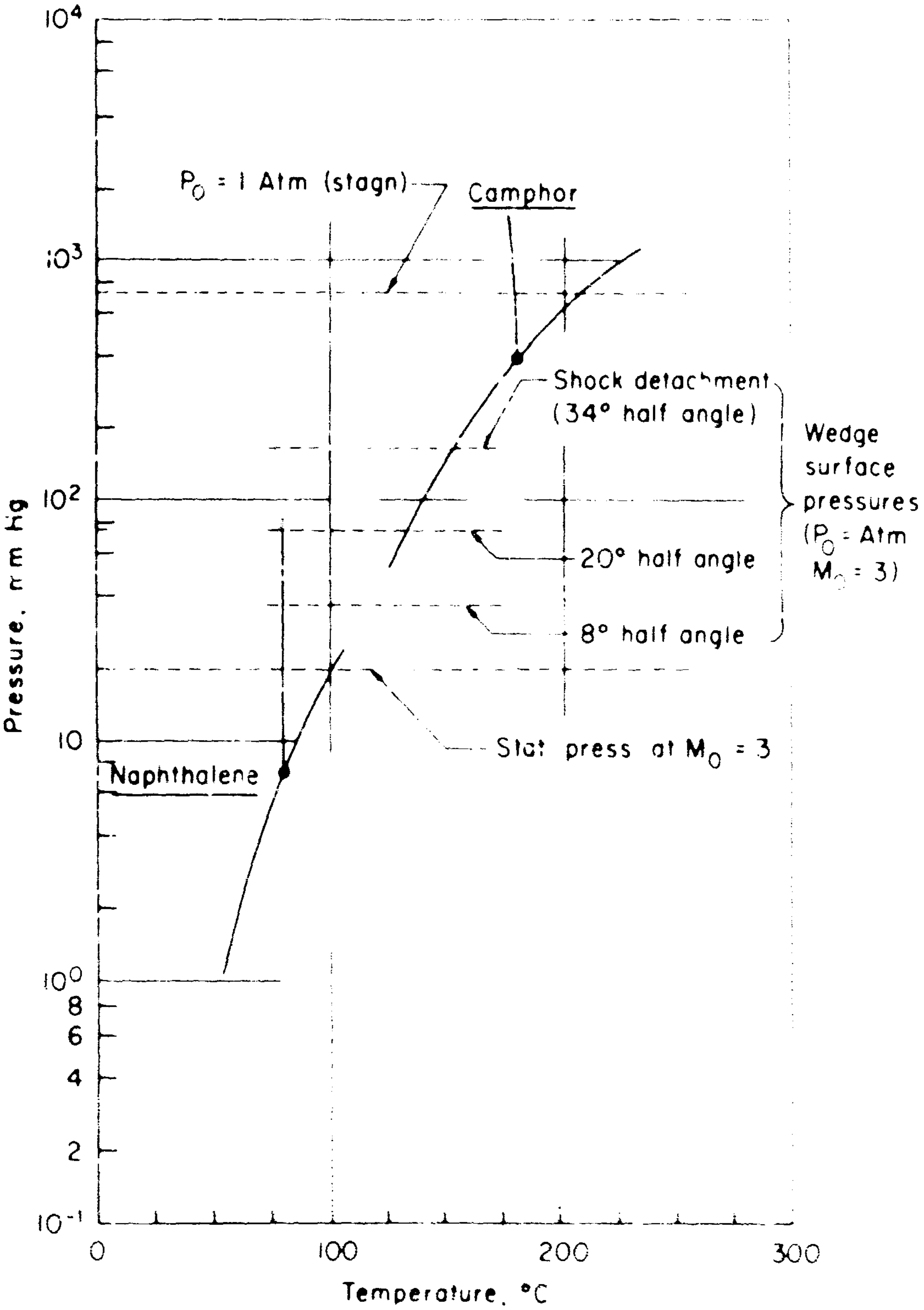

Fig 1 — Equilibrium phase-diagrams of camphor and naphthalene relative to typical pressures in a M = 3, atmospheric stagnation pressure tunnel

Table 1

APPROXIMATE BASIC PHYSICAL PROPERTIES OF CAMPHOR AND NAPHTALENE

	Camphor (d-)	Naphtalene
Formula	$C_{10}H_{16}O$	$C_{10}H_8$
Mol. weight	152.23	128.16
Cryst. form	Hexagonal	Monoclynic
Density - solid (gr/ml)	0.99	1.145
Normal boiling temp (deg C)	204	217.9
Normal melting temp (deg C)	176-177	80.22
Heat of sublimation (cal/gr)	58.5	132
Heat capacity (solid) (cal/gr deg C)	0.445	0.285
Thermal conductivity (solid) (cal/cm sec deg K)	0.96×10^{-3}	1.8×10^{-3}

3 and above.* In Ref. 2, the "equilibrium" solution is given in more detail as a function of surface temperature with static wind-tunnel pressure and recovery temperature as parameters (Figure 1c of Ref. 2). This instructive graph shows how the entire range of the sublimation problem can be covered by varying the wind-tunnel pressure between 1 and 100 mm Hg and the recovery temperature between 100 and 600°C.

One might also mention at this point that it is conceivable to extend the test potential of camphor to include gas phase reaction in the boundary layer. Camphor is highly flammable and combustion in the boundary layer seems to be sustainable, either by increasing the oxygen content of the wind tunnel air or by artificially initiating and/or flame holding the reaction. This is an interesting possibility to be investigated later in this program.

Casting Problems

Both camphor and naphthalene are anisotropic crystalline materials. Early experiments indicated that the development of a manufacturing technique which would result in satisfactorily homogeneous models, constitutes the key to the success of the use of these materials in aerodynamic study and the reliability of the results from a theoretical point of view.

In all other experiments known to the author, the models were prepared

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*The U.C.L.A. supersonic tunnel A which served for the preliminary tests discussed subsequently, operates within the range of pressures described above. In order to provide the desired stagnation temperature variation, it was equipped with a common industrial steam heat exchanger. This yields up to 100°C stagnation temperature. All tests shown subsequently, however, were conducted without using the heater, that is, at approximately room stagnation temperature.

either by direct casting at high (atmospheric) pressure or by layer casting (dipping) of a basic core in liquid material and subsequent machining or sanding to the desired shape.

We shall review our experience with these methods and describe our further attempts at sintering, rather than casting the models.

A. Recrystallized models - casting

Direct recrystallization in a mold under a variety of cooling schedules and pressures, results in the growth of relatively large crystals. These can be more or less disoriented by proper design of the boundary of the mold (the heat sink) where crystallization begins. In the present experiments attempts were made to cast cylinders with and without central stems in molds made of metal and low thermal conductivity plastics. The walls of the molds used were either smooth, which resulted in the growth of long, radially distributed crystals, or wavy in such a fashion as to initiate a disoriented growth of these crystals. However, in all cases the models were clearly crystalline in nature.

One can postulate a priori that a crystalline structure is not desirable, unless, perhaps, the crystal orientation is indeed completely random and their size is much smaller than the local thickness of the boundary layer about the model. Also, it is of course necessary that there be no voids in the mass of the body and no air pockets. Since microcrystalligraphic monitoring of the results of the castings would be impractically difficult, we selected two standard phenomenological checks by means of which different models could be studied and compared. These checks were:

a) Static Sublimation

Cylinders 1/2" in diameter and 2" long were placed in an oven maintained at atmospheric pressure at 150°F. The behavior of the model as it sublimated by natural convection was observed and recorded.

b) Wind Tunnel Tests

Several standard models, (for example, a 4:1 fineness ratio circular cone cylinders with half inch base diameters and hemispherical nose cylinders) were tested at Mach 3 (atmospheric stagnation conditions) and their behavior was again observed and compared.

The behavior of all casts (recrystallized) models, under both standard tests was found not to be satisfactory. The surface developed pronounced nonuniformities, holes and peaks, and soon became microscopically rough. In wind tunnel tests such surface roughnesses (in particular, surface depressions) tend to grow. In some cases this resulted in serious changes in the flow field, visible under the form of local shock structures. The sharp leading edge of the cone exhibited a clear tendency to break off in large chunks along prevalent crystalline surfaces, which generated local large changes in the leading edge shape, which in turn, propagated down stream in the form of deep axial grooves.

The scale of these disturbances, which seemed clearly related to the crystalline character of the model, was deemed much too large to be acceptable for the purpose at hand.

B. Dip casting (layer recrystallization)

Experiences similar to those described above have led other investigators to build models by depositing the material on the core by successive dipping in molten liquid. The initial external appearance of models produced by this method indicates fairly homogeneous mass and a fine random crystalline structure. The junction surface between successive layers is only faintly visible. The material is completely opaque.

A number of models of different types were produced by this technique and tested. The crucial test, which led us to abandon this technique, consisted of casting a cylinder by pouring thin successive layers into a cylindrical mold and subjecting it to the static oven test. The model, although the bond between the successive layers appeared to be good when cold (for instance, models were broken by shock and bending loads and did not evidence a tendency to shear along the surfaces of the layers), disintegrated into a pile of elemental "dishes" after only a few minutes in the oven. This test was repeated several times using different thicknesseses of successive layers and different rates of cooling with the same result.

This observation throws doubt upon the validity of sublimation experiments with models which were prepared in this way. (See, for instance, Ref. 3.) In these tests, the models were always spherical and the curvature of the inner layer surface provided a mechanical bond to the whole, so that the experimenters would not have the opportunity to observe the shearing between the layers when heated.

It appears probable that the behavior of the layer interfaces is caused, at least in part, by trapped and absorbed air which prevents material bond.

C. Open air sintering (undeaerated)

Next, a sintering process was tried. For this purpose, camphor was powdered and the powder was introduced into a cylindrical mold equipped with a piston. The mold and its contents could be preheated in an isothermal bath and the powder could be compressed at different rates to different final pressures (up to 40,000 psi). This is, of course, the process which is used to produce commercial products, such as, for example, naphthalene moth balls.

Sintered models have a good cold appearance. They are strong, devoid of visible crystalline structure, opaque, somewhat rough, but easily machinable. However, their behavior under test still seemed unsatisfactory and their sublimation in the wind tunnel disclosed phenomena which did not seem intuitively satisfactory.

Figure 2 shows a model produced by this technique after 15 minutes in the static oven. The surface of the cylinder is partially covered with a powder-like (loose) residue. The end cross section of the cylinder has not sublimated uniformly.

Figure 3 shows selected Schlieren photographs of a test on a blunt (hemispherical) nose cone-cylinder produced by open air sintering. This model exhibited from the start a band of material of a granular consistency on the cylindrical after-body. Patches of such consistency appeared occasionally in models produced by this method, either on the surface or within the mass of the material. They looked like a composite mass of small independent crystals with voids. The roughness, however, seemed larger than the size of the initial powder particles used.

During the test it soon became evident that the granular patch possesses

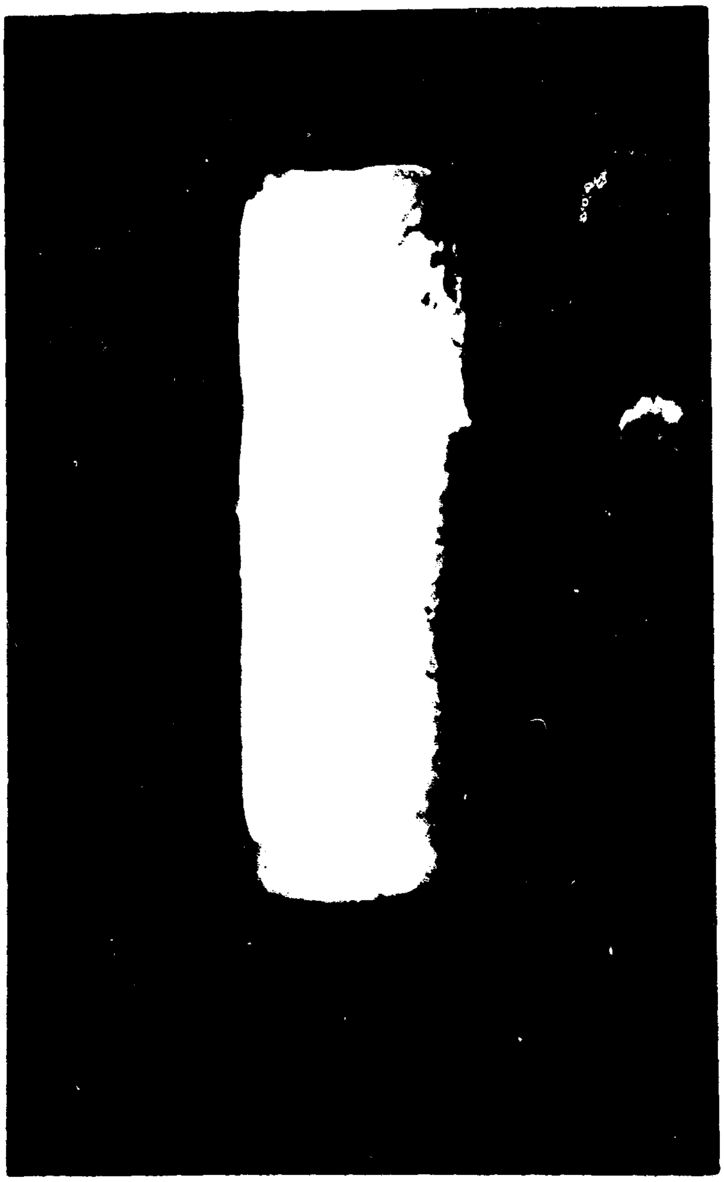

Fig. 2 — Sintered camphor model 150°F after 15 min in an oven (not pre-deaerated)

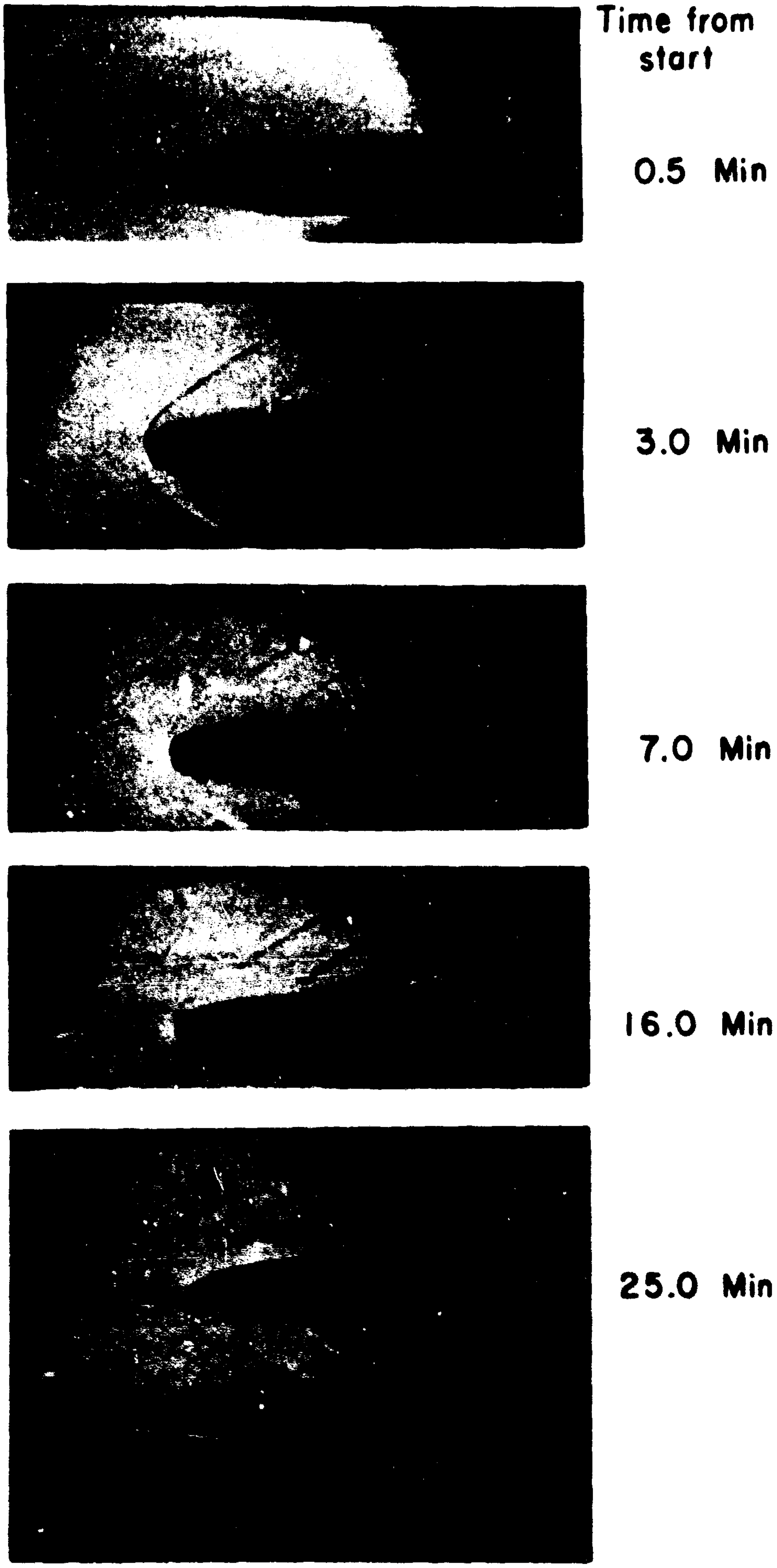

Fig. 3 — Sublimation of sintered (not deaerated) camphor hemisphere-cone-cylinder
$M = 3$, $T_{STAG} = 79°F$ $Re \sim 100{,}000$ per in.
(note behavior of "granular" patch)

entirely different characteristics than the remainder of the material. The patch shows up clearly after three minutes, remains hardly changed during most of the test (twenty five minutes in the wind tunnel, Mach 3, atmospheric stagnation conditions) and finally breaks off.

The explanation of the observed phenomenon is not clear. Whatever the aerothermal surface characteristics responsible for the behavior of the granular patch are, it is obvious that the existence of such granular masses, near or underneath the surface, is not acceptable for the study.

D. Deaerated powder sintering

The disintegration of dip cast models along the inter-layer surfaces upon heating, and the appearance of the granular patches in sintered models, suggested that the difficulty may stem from the presence of a foreign gas, (air), in the mass of camphor, both in interparticle voids and absorbed to the surface.

This suggested that before compression, the powder should be deaerated and rendered completely homogeneous chemically. A vacuum tight mold was built (shown in Fig. 4), which incorporated ducts and grooves in the internal surface of the mold through which the gas could be removed by pumping. This mold was immersed in a constant temperature bath at 212°F (boiling water). Then the powder contained in it was subjected to reduced pressure. The material sublimated because the pressure was maintained below that of the triple point at the corresponding temperature, expelling the air contained in the voids and adsorbed by the surface of the powder particles. Pumping was continued until the system pressure (upon shuting the pump off) remained satisfactorily close to the equilibrium vapor pressure

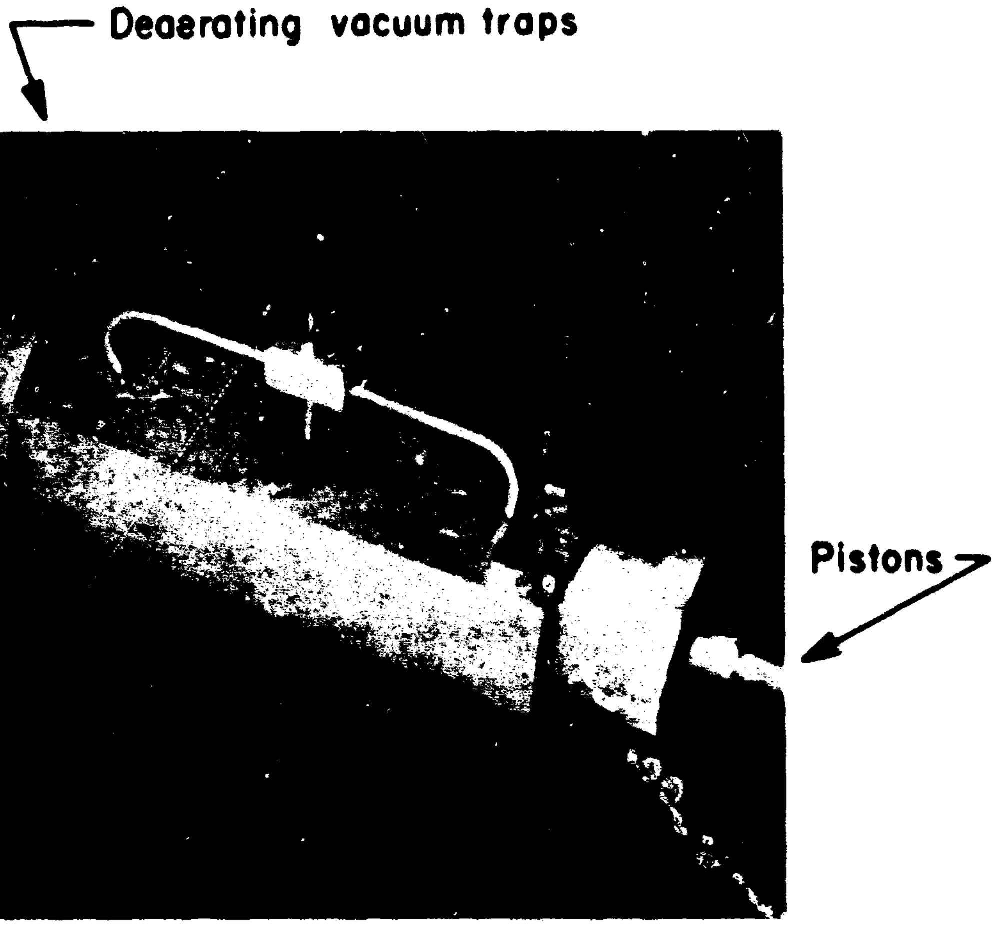

Fig. 4 — Two-piston mold for sintering camphor cylinders (1/2 in. dia 2 in. long) with provisions for deaerating prior to compression

at the bath temperature of the material. The piston was then disengaged and the powder was compressed.

The models obtained by this procedure in camphor are absolutely homogeneous and smooth. One such model, after 15 minutes in a static oven (compare with Fig. 2), is shown in Fig. 5. This picture was chosen to demonstrate the two different appearances of the material obtained during the vacuum sintering experiments. They are: (a) clear, translucent mass (b) milky white opaque mass. Both types behave in the same fashion under all the tests to which they were subjected. However, based on intuition, the clear casting will be given preference for aerodynamic studies. The milky appearance seems to be associated with the compression process. For example, the 2" long cylinder shown in Fig. 5 was produced in a mold having a single compression piston. It was produced by an impact load. The milky side of the case was adjacent to the piston; the clear side to the bottom of the mold. Furthermore, one totally clear model was cooled, suddenly, to dry ice temperature and was observed to turn milky upon cooling. This leads us to believe that the milky appearance is due to microscopic faults and cracks through the mass, resulting from nonisotropic heat properties and residual shears in the material. The two piston mold, which is shown in Fig. 4, was built as a result of these observations. This design minimizes the travel of each piston and results in a more uniform compression on the powder. Indeed, it is found that the double piston mold with pressures applied fairly gradually, in a hydraulic press up to a maximum of 5,000 lbs (for the half inch base diameter) result in reproducible homogeneous totally clear cylinders 2" long. We believe that other shapes and sizes can also be produced satisfactorily with perhaps minor adjustment in

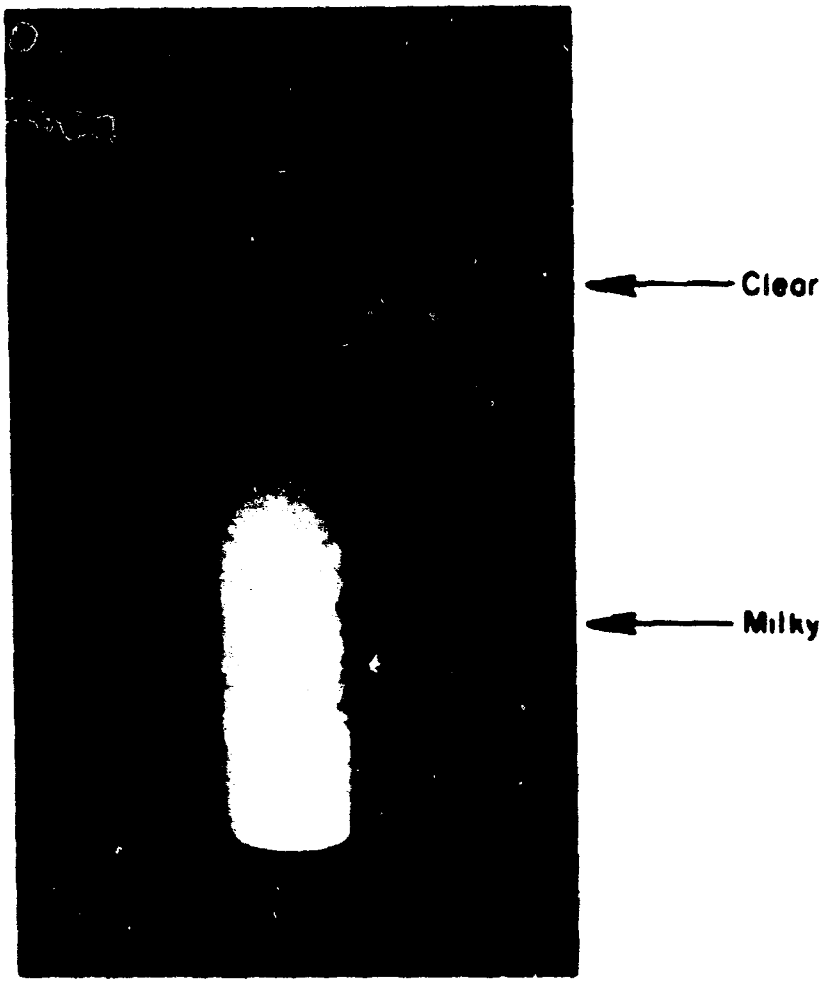

Fig. 5 — Deaerated sintered camphor model after 15 min in an oven at 150° F (produced in single-piston mold)

the design of the mold and the compression technique. The rate of pressure applied and the bath temperature seem to have very little, perhaps no influence, on the final appearance and properties of model produced by the deaerated sintering process.

Preliminary Tests and Observations

Figures 6 and 7 show two tests conducted at Mach 3 in atmospheric stagnation conditions on sharp nosed (4:1 fineness ratio) cone cylinder bodies and on the blunted (2:1 nose to after-body diameter) cone cylinder.

The primary purpose of these tests was to verify the reproducibility of the results and justify the use of vacuum sintered, clear camphor models for quantitative work. It is evident, by comparison with Fig. 3, that a large improvement over the original model was achieved and that the extreme roughness and random surface nonuniformity observed in initial tests (as well as in other programs) is not an inherent characteristic of the aerodynamic sublimation, but that it may be rather associated with the homogeniety and uniformity of the model surface.

This does not mean that the surface nonuniformity did not appear during these tests. On the contrary, qualitative observations indicated that both stream-wise grooves and cross-stream depressions are self propagating in this complex flow field. However, with the clear homogeneous models, the origin and development of these depressions is more regular and seems understandable, not like the arbitrary and nonreproducible roughening of the surface observed in the earlier tests.

Figure 8 shows, for example, a close-up photograph of the sharp leading edge of one of the conical models towards the end of the test. The stream-wise grooving is very evident. These grooves seem to be triggered

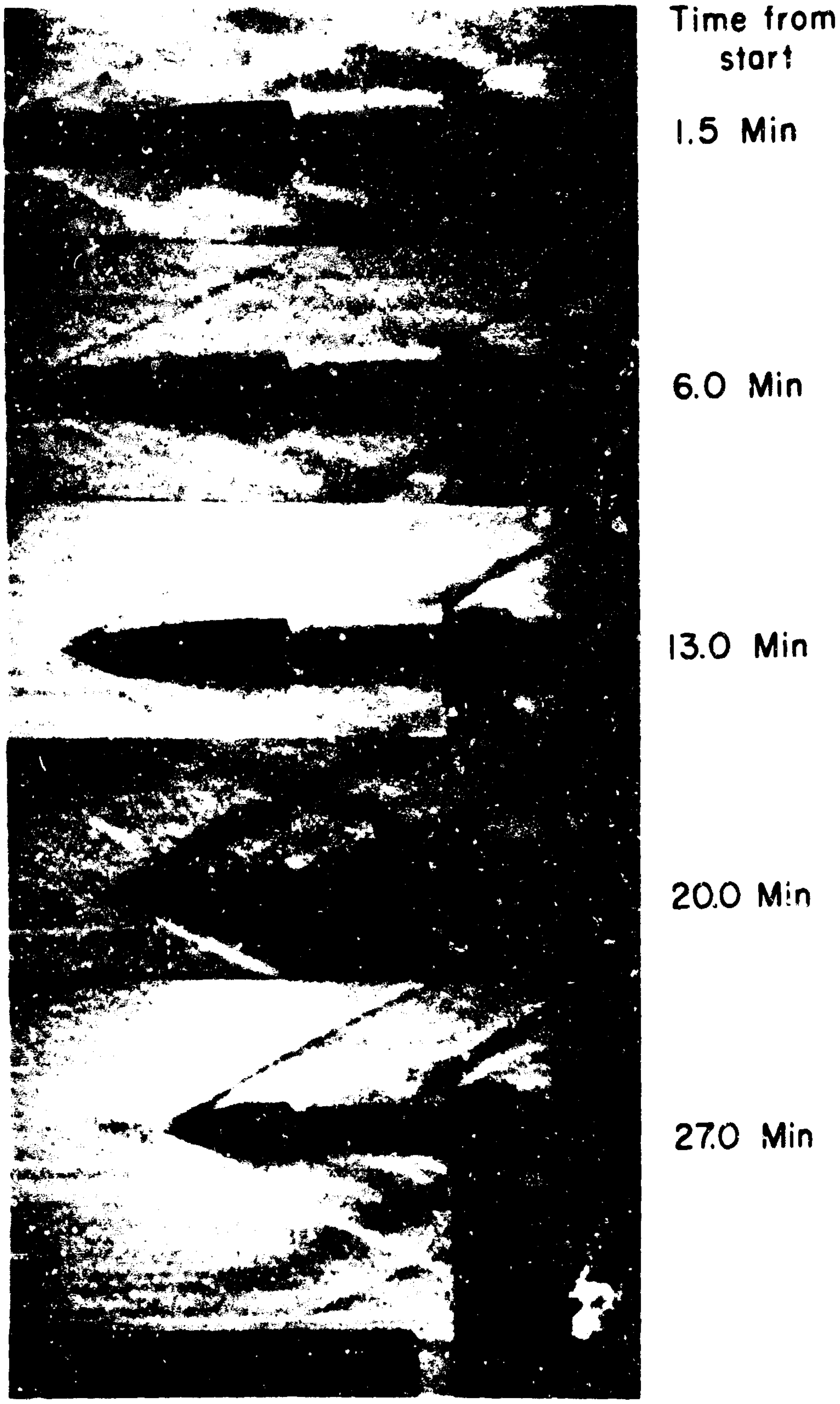

Fig. 6 — Sublimation of a camphor cone (clear) at $M = 3$, $P_0 = 1$ atm, $T_0 = 81°$ F

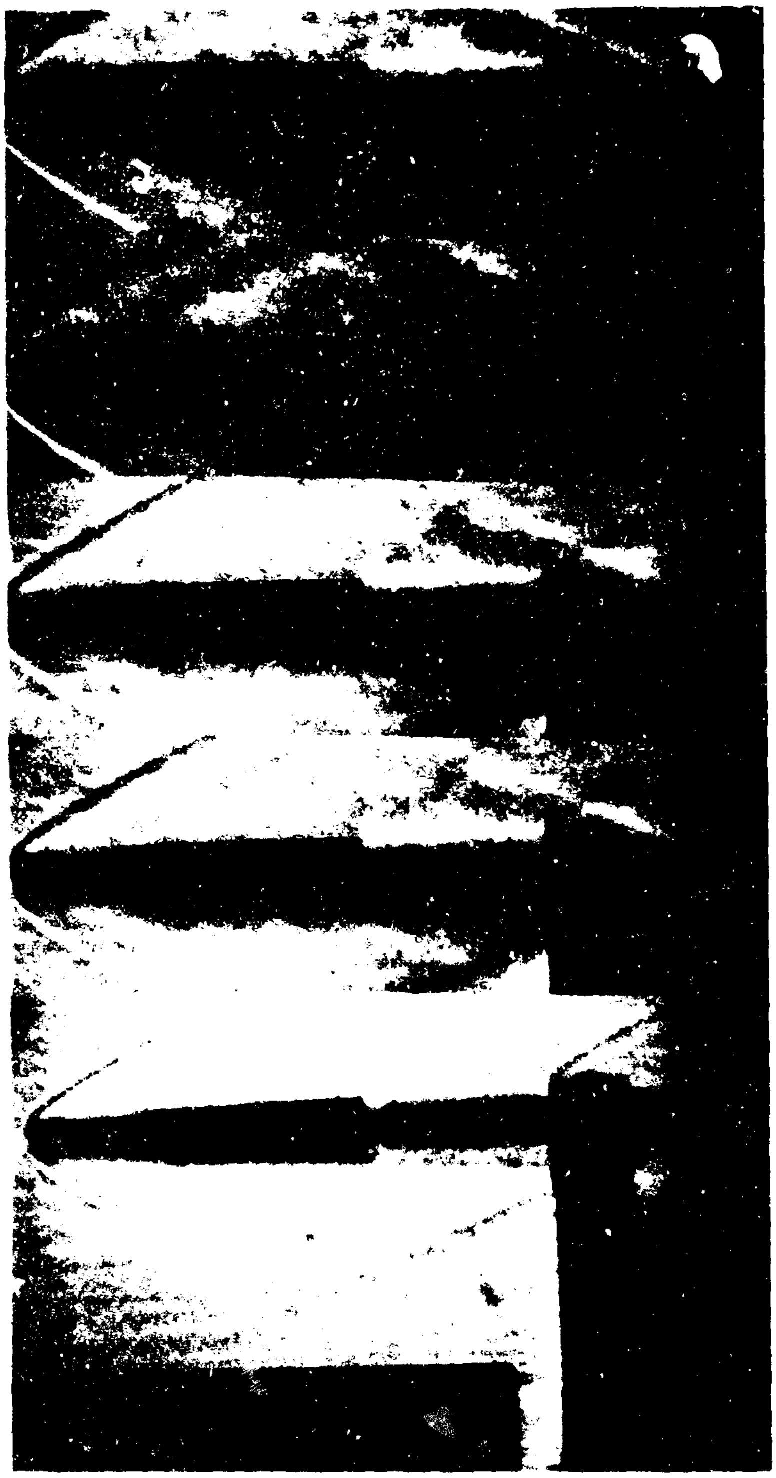

Fig. 7 —— Sublimation of a camphor blunted cone (clear) at $M = 3$, $P_0 = 1$ atm, $T_0 = 81°$ F

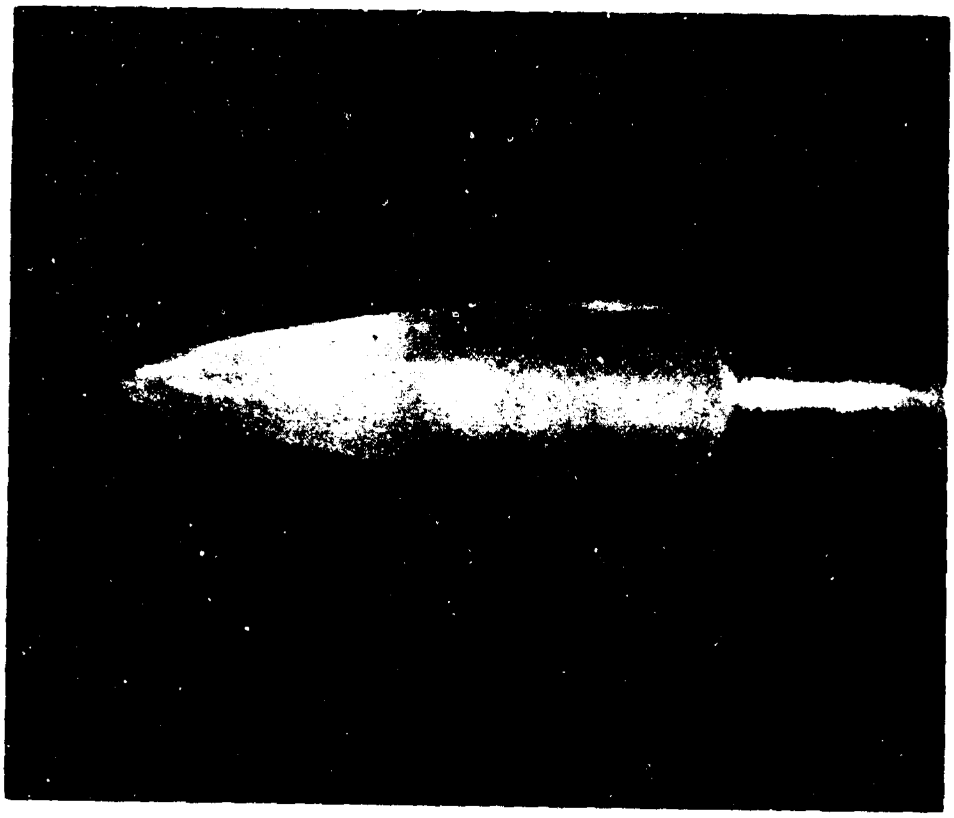

Fig. 8 — Closeup showing the streamwise grooves originating from random chipping of the sharp nose

by the fragmentation of the very tip of the sharp cone. This brings out the role played by the shear strength of the material in regions of extreme stress, such as the sharp leading edge. It is interesting to note that the stream-wise grooves seem to be bounded in their growth; that is, there seems to be an equilibrium depth of a groove beyond which it does not develop any further.

The reproducibility of the model recession rate at a given stagnation pressure and temperature was checked by repeated tests with several models of identical geometry (both clear and milky) and found to be very good.

Finally, although these preliminary tests are not intended to study the aerodynamic sublimation problem in itself, it is interesting to note the pronounced qualitative difference in the equilibrium shape of the two related geometries tested. The cone with a sharp leading edge sublimated to a near conical, but concave shape, while the blunted cone was reduced instead to a blunt cylinder followed by a convex transition shape to the second cylindrical after-body.

Measurement of Surface Temperature

It is essential to measure in fair detail the surface temperature during the course of sublimation testing, in order to make valid quantitative calculations and comparisons with theory. In models recrystallized from a fused liquid, it is relatively easy to cast in thermocouple junctions and obtain some indication of the temperature. This is not very satisfactory, because it is difficult to interpret the readings in terms of surface conditions (while the thermocouple is embedded, its position is relatively poorly known) and after the surface has sublimated past the junction, it disturbs the flow. Finally, only relatively few such thermocouples can be cast into a reasonable size wind tunnel model.

Different methods were sought through the literature. This led to the selection of a type of spectroscopic optical measurement which appears to offer remarkably good sensitivity and a possibility of a practically unlimited detail in the measurement of surface temperature without disturbing the flow. The development of an apparatus is currently under way.(1)

For this purpose, a powdered fluorescent material (for instance, cadmium sulphate) is mixed in with the camphor prior to sintering. Experiments to determine the minimum percentage of this indicator in the camphor are under way. It seems that the required fraction of this foreign material is sufficiently small (and the particle size is sufficiently small) so that the exposure of the indicator grains to the air stream as the material sublimates, does not result in disturbing the flow; particles are simply carried off by the boundary layer. The instrument consists of the following: an optical system focuses a beam of ultraviolet exciting radiation on a small area on the surface of the model, the temperature of which is to be measured. Another optical path looks at the resulting fluorescence. Use is made of the temperature sensitive characteristic of this emission (see Refs. 4, 5, and 6).

The basic law of fluorescent emission is given by the Gaussian equation

$$I = A \exp \left[-B (\nu - \nu_0)^2 \right] \qquad (1)$$

where I = intensity of fluorescent emission

A,B = spectral distribution constants

ν = frequency of emission

where A, B and ν_o are temperature sensitive parameters. The amplitude factor A depends also on the spectrum of the exciting radiation and on the surface density of the active material. Since these factors are not known accurately, an absolute measurement of the intensity of the fluorescence is not a good temperature indicator. Two relative intensity measurements can, however, be suggested instead. They are:

$$\alpha_1 = \frac{I(\nu_1)}{I_T} = \frac{I(\nu_1)}{\int_o^\infty I \, d\nu} = \left(\frac{B}{\pi}\right)^{1/2} \exp\left[-B\,(\nu_1 - \nu_o)^2\right] \qquad (2)$$

α_1 is a relative intensity of emission in a narrow band of the total luminosity. Also,

$$\alpha_2 = \frac{I(\nu_1)}{I(\nu_2)} = \frac{\exp\left[-B(\nu_1 - \nu_o)^2\right]}{\exp\left[-B(\nu_2 - \nu_o)^2\right]} \qquad (3)$$

α_2 is the relative intensity of the emission at two distinct frequencies.

Both α_1 and α_2 contain temperature sensitive constants B and ω_o, which cannot be accurately described by theory. Consequently, the instrument must be experimentally calibrated. However, neither α_1 nor α_2 depend on the local density or on the excitation of the fluorescence. α_2 can be expected to be more reliable as an indicator than α_1, because it is less sensitive to B and through it, to spurious effects such as the spectrum of the exciting radiation.

Figure 9 shows the relative spectral distribution of cadmium sulphide at various temperatures excited by ultraviolet radiation. Figure 10 shows the ratio α_2, which is the proposed temperature indicator for this research,

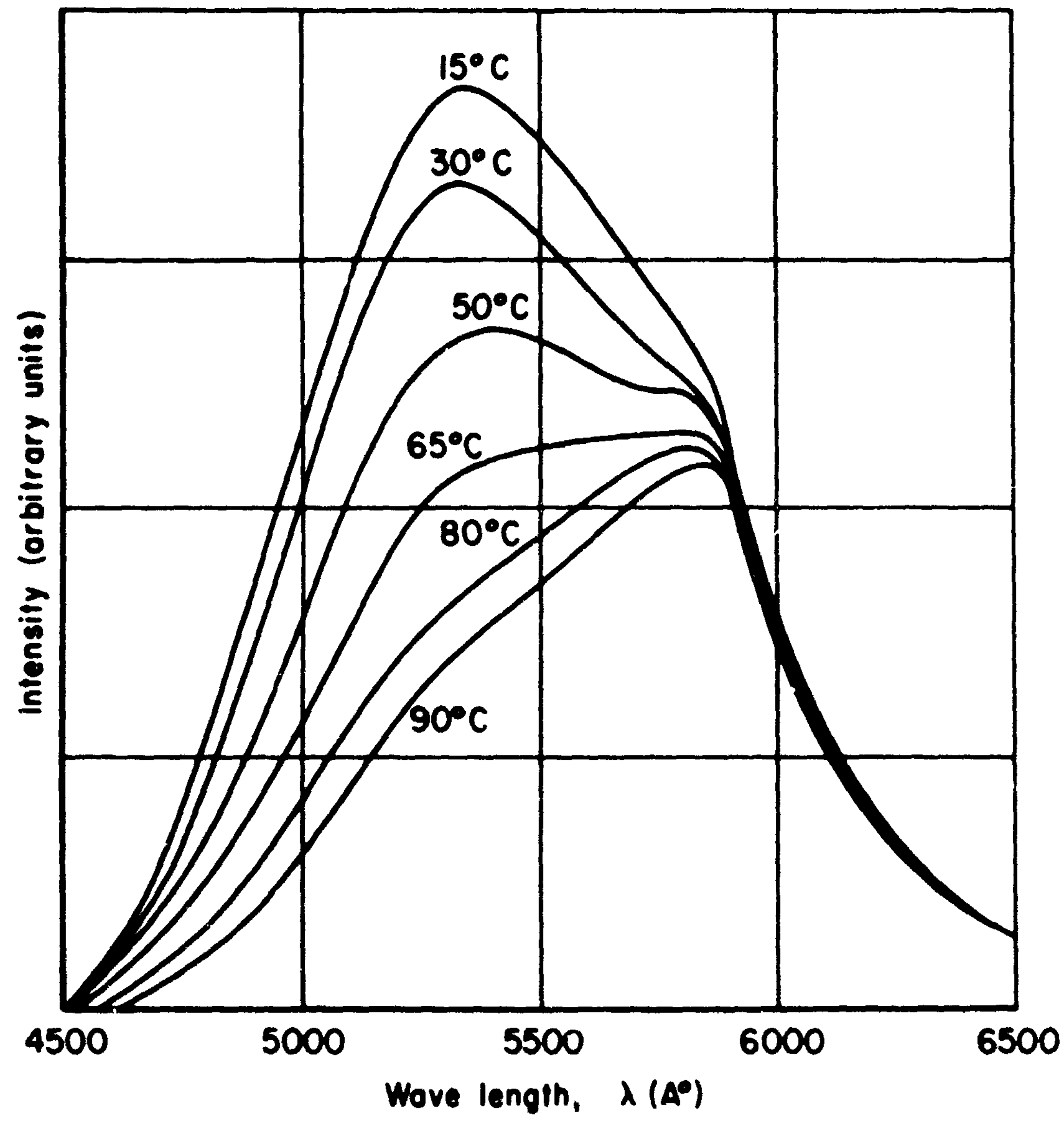

Fig. 9 — Spectoral distribution of the fluorescence of cadmium sulphate as function of its temperature

(P. Thureau, Note: techn. min. air (France) 73, 1958)

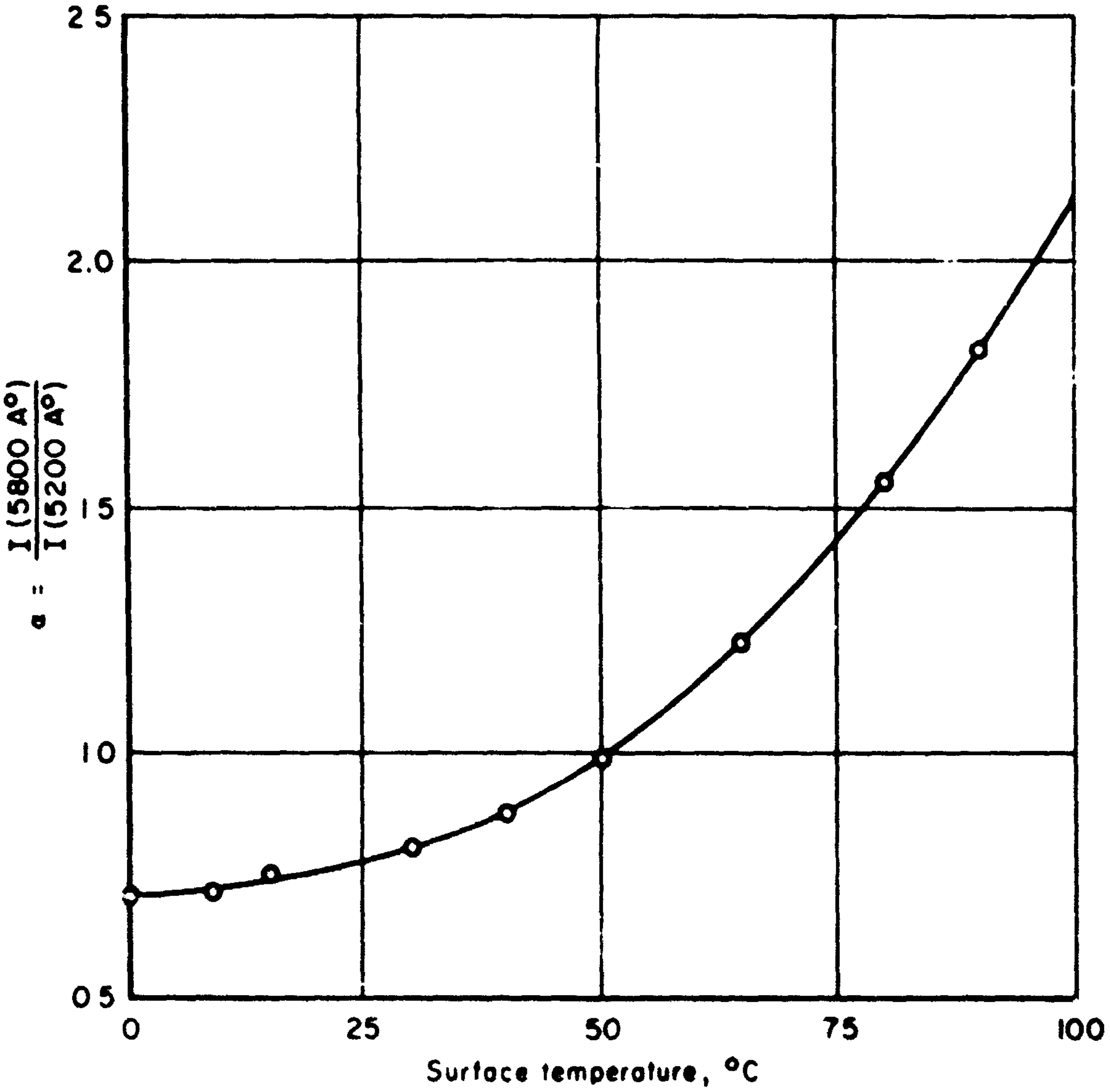

Fig. 10 — Calibration curve of the relative intensity of emission at 5800 and 5200 angstroms cadmium sulfide

(From P Thureau)

formed by measuring the relative intensity of two distinct wave bands as a function of surface temperature. The optical equipment to achieve this is very simple, consisting merely of a prism to split the fluorescent light and make it go through two colored filters which absorb all but the desired wave bands. The two light paths are then thrown upon two photo cells and the output of the photo cells is compared. The calibration curves shown in Fig. 10, which is taken from Ref. 4, is obtained from a sample made by mixing cadmium sulphide powder with ordinary glue and painting it upon a metal surface.

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