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PHASE CHANGE INDICATORS FOR SUBAMBIENT TEMPERATURES

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TEMPIL° CORPORATION
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SUMMARY

Forty candidate organic compounds were evaluated as possible fusible temperature indicators for use in the range -50°F to -150°F. Of these, thirty with melting points ranging from -37°F to -162°F were found to be useful as temperature indicators. Nine candidates were rejected because they did not yield opaque, crystalline coatings by any of the application procedures attempted. One candidate material was rejected because it proved to be unstable. Phase studies of several binary systems were also carried out.

A number of application procedures were evaluated. An aerosol-spray procedure was adopted because it consistently yielded opaque coatings, was relatively simple to employ and could probably be adapted for use in the Langley Field test apparatus.

The indicators were found to signal properly at a reduced pressure of 2mm mercury, as well as at sea-level barometric pressure.

INTRODUCTION

In the July 1964 issue of the Journal of the American Institute of Aeronautics and Astronautics, Messrs. Robert A. Jones and James L. Hunt of the NASA Langley Research Center published a paper captioned "Use of Temperature-Sensitive Coatings for Obtaining Quantitative Aerodynamic Heat Transfer Data".

This paper described the use of Tempilaq° phase-change temperature indicators for obtaining accurate heat-transfer data on models of complex shape in wind tunnel tests. All of the work described was carried out using temperature indicators having ratings above 100°F, the lowest temperature for which these materials are commercially available.

In a letter of March 4, 1965 Tempil° Corporation proposed to undertake the development of phase-change indicators which could be used to extend this technique to temperatures well below the normal climatic range. NASA Contract NAS1-5667, dated December 9, 1965, authorized an investigation to develop materials and corresponding application techniques

that could be used as phase change temperature indicators in the temperature range of -50°F to -150°F, and would be suitable for aerodynamic heat transfer testing by the method described in the Jones and Hunt paper referred to above. The indicators would be used at environmental pressures ranging from 2mm Hg to one atmosphere.

The following desired characteristics of the indicators were outlined in the contract to serve as development guidelines:

    a. The phase change of the indicators should be clearly visible so that it can be recorded with black and white film.

    b. The indicating temperature should be unaffected by ambient pressures from 2mm Hg to one atmosphere.

    c. The indicating coating should have a very short response time so that the phase change temperature will be unaffected by the heating rate.

    d. The method for applying the indicator should be such that repeatability of results can be obtained.

    e. The indicators should have a low order of toxicity and should be chemically inert.

LITERATURE EXPLORATION -   The target properties -- melting point range, low vapor pressure, long-term stability, inertness and low order of toxicity -- appear to have fairly well restricted the chemical compounds available as candidate temperature indicators. Examination of the literature revealed that two classes of organic compounds, esters and aromatic hydrocarbons, offered the most promising, readily available candidates. Our own experience with esters at elevated temperatures (over 100°F) led us to believe that this class of compounds might also have the necessary crystallization properties, i.e., little or no tendency to supercool below the freezing point and a strong tendency to form opaque, clearly visible crystals -- as opposed to the formation of glasses which would be undesirable.

Aromatic ethers, cyclic aliphatic ketones and aliphatic alcohols were other classes of organic compounds which offered several additional candidate materials.

SOURCE OF CANDIDATE MATERIALS -   All candidates for fusible temperature indicators actually used in this work project were the best grades available from Distillation Products Industries, Eastman Organic Chemicals Department, Rochester, N.Y. 14603. All are listed in the current D.P.I. catalog, and were evaluated without further purification or treatment.

LOW-TEMPERATURE TEST CHAMBER -   The test chamber used throughout this work program was an eight cubic foot (2' x 2' x 2') capacity Model WF-8-175V

Low Temperature Environmental Chamber manufactured by the Webber Manufacturing Company, Inc., Indianapolis, Indiana.

Air in this chamber was circulated by a fan and air temperatures were adjustable from ambient to -175°F. Provisions were available for evacuating the chamber to pressures of less than 2mm Hg. On each of the two sides of the chamber was a 2-inch service port through which electrical leads, tubes or probes could be introduced.

The side-hinged, overlapping door on the front of the chamber was supplied with two 6-inch port holes for glove and/or hand insertion and manipulation of articles within the chamber under atmospheric pressure conditions. These ports were flanged and could be sealed if the chamber was to be evacuated. The door was also equipped with a 12" x 12" observation window consisting of a special hermetically sealed 6-pane thermal glass assembly.

SCREENING OF CANDIDATE MATERIALS -   Initial attempts to evaluate candidate materials involved observation of small quantities of liquid in glass test tubes and in capillaries. This method was found unsatisfactory because it was difficult to observe changes of state which might have taken place and because the length of time necessary for the relatively large quantities of liquid to reach thermal equilibrium with the air was found to be excessively long.

After some experimentation, the following procedure was adopted and used in the initial screening of most of the candidate materials:

A drop or two of fluid was placed in the center of a 75x25mm glass microscope slide and covered with an 18mm cover slide, thus sandwiching a thin layer of material between glass surfaces. This glass sandwich was then placed on a wooden rack in an almost vertical position. The rack was painted black to form a dark background. Illumination was provided by four $7\frac{1}{2}$ watt bulbs, two on each side of the rack. The chamber was then cooled until crystallization of the candidate occured or until a temperature of -175°F was reached.

Using this set-up, results were easily observed and phase-changes from liquid to solid, when accompanied by the formation of opaque white crystals, was very dramatic against the black background.

The above method was relatively simple and enabled us to evaluate several samples at once. Results obtained were thought to correlate well with those which would be obtained under the anticipated end-use conditions.

AEROSOL APPLICATION OF INDICATOR MATERIALS -   The following aerosol application method was developed as a consequence of our search for a final form for the temperature indicators and corresponding practical method for applying them. It was used principally for the final temperature calibration of the indicators, although it would also have been an excellent means

for initially evaluating the crystallization properties of each material -- the evaluation carried out on almost all of the candidates by the microscope-slide method described in the previous section.

In employing this procedure, the substrate was cooled to a temperature below the melting point of the indicator. In the case of readily crystallized materials, cooling the substrate to approximately thirty degrees Fahrenheit below the melting point of the indicator was sufficient. In other cases, cooling with liquid nitrogen to temperatures approaching -300°F was found necessary.

A six-ounce aerosol container containing 60 grams of the indicator liquid and 75 grams of Freon 12 propellant -- no solvent -- was then inserted into the test chamber through one of the port holes and a spray was directed onto the cooled test piece from a distance of six to eight inches. The aerosol containers were stored under ambient conditions prior to use, but apparently cooling of the indicator particles by evaporation of the Freon 12, by passage through the cold atmosphere of the chamber, and, finally, by contact with the cold substrate was sufficient to yield a white, opaque, adherant, solid coating several thousandths of an inch thick.

All applications of indicator coatings by this method were carried out under atmospheric pressure conditions. When calibrations were to be carried out in a vacuum, application was followed by sealing of the chamber and evacuation.

UNSUCCESSFUL APPLICATION FORMS AND PROCEDURES

Suspensions of materials in a volatile vehicle (Tempilaq°) -   Most of the indicator candidates studied are excellent solvents for organic compounds. Because of this, the choice of fluids available as insoluble, volatile fluids for dispersion of the candidates was severely limited. After discarding water because of its high melting point, the remaining possibilities were narrowed down to aliphatic hydrocarbons or some of their fluoro- and chloro-substituted derivatives (Freons).

Several suspensions were made up in hexane, the most volatile aliphatic hydrocarbon available which was a liquid under standard atmospheric temperature and pressure conditions. The most serious problem encountered was the lack of volatility of the vehicle at the low temperature employed in this investigation. At a temperature of -100°F, hexane showed no tendency to evaporate. Results were the same whether application was by brush or aerosol spray. This was not completely unexpected, and confirmed expectations that it might be necessary to employ compressed gases such as methane, ethane or one of the more volatile Freons as a vehicle. This would have involved some means of suspension of the liquid at ambient temperatures, followed by a procedure for converting this suspension to a dispersion of fine crystals on cooling to below the indicator's melting point. Alternatively, developing a low-temperature milling procedure for forming the dispersions directly from the solidified indicator and solvent would have been necessitated. No work beyond the several hexane dispersions was carried out.

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Brushing of Super-Cooled Pure Liquids - By carefully cooling some indicator liquids to temperatures below their melting points, it was possible to brush-apply these super-cooled indicators onto a cooled substrate. The disturbance caused by brushing the indicators onto the surface was usually sufficient to cause instantaneous crystallization on the surface. The coatings which were opaque were also extremely uneven, and made up of rather large crystals and lumps. Furthermore, premature crystallization of the bulk prevented coating more than one or two square inches of surface during any one experiment.

Aerosol Application of Pure Indicators Cooled to below their Melting Points - Prior to the use of pure indicators in aerosol containers stored at room temperatures by the method described above, cooling and storage of aerosol containers at temperatures which ensured crystallization of the indicator was attempted. Excessive hardening of the spray valves, severe reduction of Freon 12 pressure and the formation of excessively large indicator crystals in the container -- all caused by cooling to the low temperatures of our experiments -- posed problems which were resolved by resorting to room temperature storage of the aerosol containers.

TEMPERATURE MEASUREMENT - The Webber test chamber, described above, was used with a Model 104NY platinum resistance thermometer (.084 inch diameter) purchased from the Rosemount Engineering Company, Minneapolis, Minnesota. Connecting this probe to the Speedomax H controller, after making the appropriate changes in the circuitry of the controller, provided a low-lag, sensitive temperature measuring system.

Accuracy of the L&N Speedomax H recorder is $\pm$ 0.3% of the temperature span; for our recorder this would be 0.83°F. The readability of this instrument is approximately 0.5°F. Accuracy of the platinum resistance thermometer, calibrated by Rosemount Engineering Co., was better than 0.28°F. All calibrations carried out by Rosemount are traceable to N.B.S. standards.

CALIBRATION OF TEMPERATURE INDICATORS - Candidate materials which froze readily, i.e., supercooled less than 30°F below their melting points, were calibrated by the following procedure:
    A one-inch square of heavy gauge aluminum foil was perforated and slipped over the tip of the horizontally oriented resistance thermometer. With the tip of the thermometer pointing toward the observer, the face of the aluminum test piece hanging from it also faced the observer. (See sketch in Appendix F.) After cooling the aluminum test piece and thermometer to below the anticipated melting point, a coating of the indicator material was sprayed onto the aluminum by the aerosol procedure described above. The environmental chamber was then allowed to warm up slowly until melting was visually observed.

The heating rate of the chamber was less than one degree Fahrenheit per minute. This low rate of temperature rise ensured thermal equilibrium

between the air, test piece and temperature probe, and avoided any dependence of the observed melting points on the heating rate.

Considering the accuracy of the instrumentation and the reproducibility of the recorded melting points, the average (2 to 4 determinations) values obtained by this method, and tabulated in Appendix A for seventeen indicator materials, are probably accurate to within plus or minus 2°F.

Candidate materials which did not readily form opaque coatings by spraying onto a surface at -175°F or higher were calibrated by the following procedure:
A circular phenolic specimen (diameter 1¼", weight 15 grams) was cooled to a temperature approximately 50°F below the expected melting point (or to -175°F) and then dipped into liquid nitrogen and held submerged for several minutes. Immediately upon removing from the liquid nitrogen, the specimen was sprayed with the indicator. After allowing approximately fifteen minutes for the temperature of the test piece to come to equilibrium with the air in the chamber, the temperature was allowed to rise slowly until melting occured.

The phenolic specimen was suspended approximately 3 inches below the platinum-resistance temperature probe during the calibration procedure. By means of a calibrated copper-constantan thermocouple, it was determined that the air in the vicinity of the test piece was within one degree of the temperature of the platinum-resistance probe. Because of this slight possible temperature variation, a possible temperature lag of uncertain proportions caused by the bulk of the phenolic specimen and a slightly higher rate of temperature rise, it is estimated that the accuracy of the values obtained by this method and tabulated in Appendix B for thirteen indicator materials is plus or minus 5°F.

EFFECTS OF VACUUM - The contract stipulated that the calibration of the temperature indicators was to be carried out under vacuum conditions as low as 2mm Hg as well as under ambient pressure conditions.

Thermodynamic considerations (Clapeyron equation) and actual experience with hundreds of organic and inorganic compounds have shown, however, that the melting point change resulting from a one-atmosphere pressure change, the maximum possible in going from atmospheric conditions to a complete vacuum, is of the order of hundredths of a degree -- a negligible consideration in view of the discussions of the existing experimental errors in the various sections above.

Nevertheless, the seventeen indicators listed in Appendix A were re-calibrated at a pressure of less than 2mm Hg. The results are tabulated in Appendix C. Considering the normal experimental error under atmospheric conditions and the absence of an air-bath to facilitate thermal equilibrium

between the aluminum test slide and the temperature probe, the observed differences between the values in Appendixes A and C are not significant.

Of significance are the facts that none of the indicators sublimed before melting, and that they all appeared quite stable, exhibiting no signs of boiling or gas evolution, upon melting.

All of the temperature indicators listed in Appendix B were also evaluated under vacuum conditions for sublimation before melting and stability after melting. None of these indicators sublimed before melting or showed signs of decomposition or evaporation upon melting. Determination of melting points was not attempted because there was no possibility of thermal equilibrium between the temperature probe and the plastic test piece under the existing vacuum conditions.

BINARY MIXTURES -   Some work was carried out to determine the feasibility of using mixtures of candidate materials with satisfactory supercooling, freezing and crystal-opacity properties in order to obtain lower melting indicators with similar satisfactory properties. Three binary systems were evaluated.

Two ester mixtures, Ethyl Octanoate/Methyl Octanoate and Hexyl Acetate/ Heptyl Acetate, were found to yield easily frozen systems with melting points closely following a classical phase-rule curve for a binary system. Melting points values for these systems were tabulated in the progress report of June 26, 1967, but they are not repeated here because the temperature measurement methods used during these evaluations were less refined than the one described above for the calibration of the single component indicators and the recorded melting points are undoubtedly in error. The eutectic mixture of the Octanoate system melted approximately 15°F below the melting point of the lower melting component while the Acetate system eutectic melted approximately 9°F below the melting point of the lower-melting component.

A system of aromatic hydrocarbons, p-Cymene/m-Xylene, was found to yield mixtures which could not be frozen by any of the methods used.

REJECTED CANDIDATE MATERIALS -   Of the forty candidate materials evaluated, ten were rejected. Nine of these could not be made to yield opaque, solid coatings by any of the methods described above. One, Dimethoxybenzene, appeared to be unstable. It froze readily, but its melting point decreased during storage, indicating the formation of a contaminating diluent, and its coatings bubbled vigorously upon melting, contrary to the behavior of the thirty useable candidates. The ten rejected materials are listed in Appendix D.

REFRACTIVE INDEX MEASUREMENTS -   At the outset of this work program, it appeared that refractive index measurements might provide a simple, room-temperature method for determining the suitability of a new lot of some particular indicator material. A Bausch & Lomb, Model 9935-A20, Abbe-3L Refractometer thermostatted at 77°F (25°C) was used to obtain the refractive index of each of the indicators listed in Appendixes A and B. These

refractive indexes are tabulated in Appendix E.

While there has been no justification to date for carrying out a work program designed to correlate refractive index values with melting point values for any of the indicators, interest in one or more of them in the future might justify additional work along these lines.

CONCLUSIONS

1. Fusible temperature indicators for the temperature range -50°F to -150°F having the target properties outlined in the introductory section can be obtained from several classes of organic compounds -- mainly, however, from organic esters.

2. Packaging in an aerosol spray container in conjunction with one of the application procedures outlined in the report appears to offer the simplest, most useful and most versatile application form of these indicators.

APPENDIX A

TEMPERATURE INDICATORS-MELTING POINT DATA

	MELTING POINT (°F)
Anisole	-37
Ethyl Benzoate	-38
Methyl Octanoate	-38
Ethyl Octanoate	-52
m-Xylene	-56
n-Heptyl Acetate	-60
Pentyl Hexanoate	-62
Diethyl Malonate	-65
Cyclopentanone	-67
tert.-Butylbenzene	-78
Hexyl Acetate	-89
Hexyl Formate	-91
p-Cymene	-97
n-Pentyl Propionate	-102
Pentyl Butyrate	-103
Methyl Hexanoate	-104
Pentyl Formate	-105

APPENDIX B

TEMPERATURE INDICATORS REQUIRING COOLING OF SUBSTRATE WITH LIQUID NITRÓGEN

MELTING POINT DATA

	MELTING POINT (°F)
1,2,4- Trimethylbenzene	-59
Mesitylene	-76
Ethyl Propionate	-107
sec.-Butylbenzene	-114
Propyl Propionate	-114
Isobutyl Isobutyrate	-118
n-Butylbenzene	-132
n-Butyl alcohol	-139
Butyl Butyrate	-139
Methyl Valerate	-139
Ethylbenzene	-143
Ethyl Valerate	-147
Ethyl Butyrate	-161

APPENDIX C

TEMPERATURE INDICATORS
MELTING POINT DATA IN VACUUM

	MELTING POINT (°F)
Anisole	-36
Ethyl Benzoate	-38
Methyl Octanoate	-39
Ethyl Octanoate	-52
m-Xylene	-56
n-Heptyl Acetate	-60
Pentyl Hexanoate	-64
Diethyl Malonate	-65
Cyclopentanone	-66
tert.-Butylbenzene	-75
Hexyl Acetate	-88
Hexyl Formate	-88
p-Cymene	-97
n-Pentyl Propionate	-102
Pentyl Butyrate	-101
Methyl Hexanoate	-102
Pentyl Formate	-102

APPENDIX D

REJECTED CANDIDATE MATERIALS

n-Butyl Formate

n-Butyl Propionate

Cumene

m-Dimethoxybenzene

Ethyl Isovalerate

Isobutyl Propionate

Methyl Cyclohexane

3-Methyl Cyclohexanone
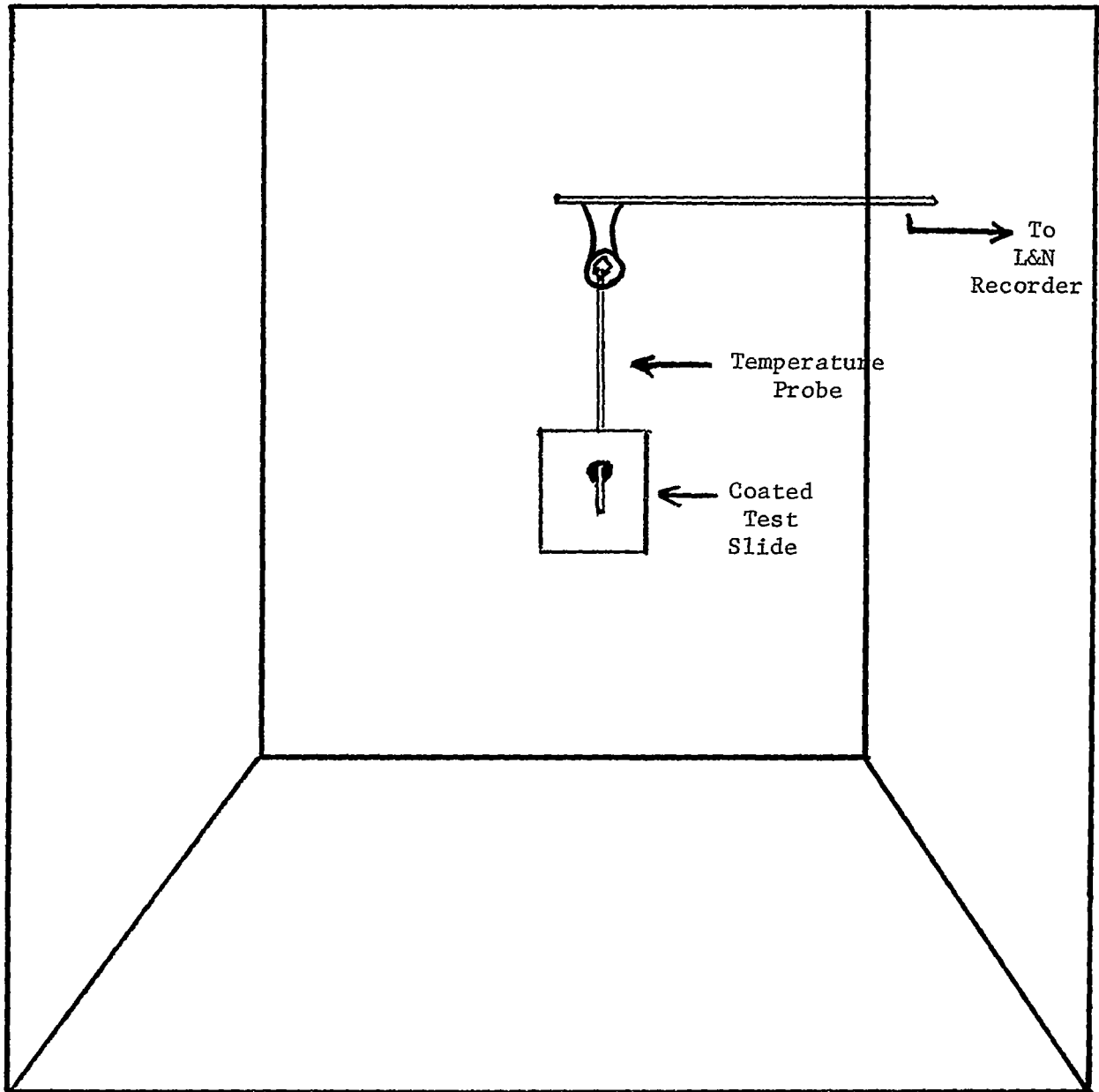
iso-Pentyl Alcohol

Propyl Butyrate

APPENDIX E

REFRACTIVE INDEX OF INDICATORS @77°F (25°C)

	REFRACTIVE INDEX
Anisole	1.5155
n-Butyl Alcohol	1.3978
Butyl Benzene	1.4882
sec.-Butyl Benzene	1.4884
tert.-Butyl Benzene	1.4907
Butyl Butyrate	1.4046
iso-Butyl iso-Butyrate	1.3975
Cyclopentanone	1.4353
p-Cymene	1.4886
Diethyl Malonate	1.4117
Ethyl Benzene	1.4938
Ethyl Benzoate	1.5032
Ethyl Butyrate	1.3906
Ethyl Octanoate	1.4165
Ethyl Propionate	1.3822
Ethyl Valerate	1.3987
n-Heptyl Acetate	1.4130
Hexyl Acetate	1.4077
n-Hexyl Formate	1.4056
Mesitylene	1.4975
Methyl Hexanoate	1.4042
Methyl Octanoate	1.4153
Methyl Valerate	1.3958
Pentyl Butyrate	1.4104
Pentyl Formate	1.3972
Pentyl Hexanoate	1.4196
Pentyl Propionate	1.4066
Propyl Propionate	1.3912
1,2,4- Trimethylbenzene	1.5025
m-Xylene	1.4957

APPENDIX F

TEMPERATURE INDICATOR CALIBRATION UNIT

To
L&N
Recorder

Temperature
Probe

Coated
Test
Slide

Front of Chamber