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1. Introduction

Fires in various types of fibers during shipment and storage have not been uncommon over the years. The major difficulties have been experienced in the handling of cotton, wool, and jute, and the heating characteristics of those fibers have been the subject of considerable study. In general the so-called "hard fibers" such as hemp and sisal, used in the manufacture of cordage, have not been considered particularly liable to self-heating and have not been as thoroughly investigated. Hemp is known to heat to the point of fiber damage very quickly after wetting, however, and there have been fires in baled sisal storage which suggest that "spontaneous" or self-heating may become a problem in large quantity stockpiling.

One such fire occurred in 1963 in cordage fibers, stockpiled by the General Services Administration near Cincinnati, Ohio, which had become rain-soaked when the building roof was lost in hurricane winds. The fiber stock was covered with tarpaulins to protect it from further weather exposure and about ten days later fire developed in the storage. To help determine and understand the cause of the fire, the National Bureau of Standards was asked to investigate some of the heating characteristics of the types of fibers included in the storage.

2. Materials and Characteristics Studied

The General Services Administration provided samples of four different cordage fibers for study. Three were labelled abaca fibers and identified respectively as Davao, non-Davao, and C. A. Light. The fourth was identified as Haitian dry sisal.

Information on the tendency of the fibers to heat spontaneously, and on the heat which might be produced upon wetting them, appeared to have an important bearing on the problem. Furthermore, from the data developed in determining the self-heating tendency of a material it is possible to estimate, for a given surface (or ambient) temperature, the critical size of a storage pile beyond which there may be a hazard of self-ignition. Accordingly, determinations were made of the heats of wetting and of the self-heating tendencies of the four fibers submitted, and a few additional points were explored briefly.

3. Heat of Wetting Determinations

The absorption of moisture by cellulosic fibers results from the affinity between water molecules and the free hydroxyl groups in the cellulose structure and is directly related to the proportion of amorphous material in the cellulose chain. It is an exothermic process and the amount of heat evolved will vary with the particular fiber considered, and also with the amount of moisture already present in the fiber and the amount of moisture absorbed. The heat of wetting may be defined as the heat evolved when the material is completely wetted with a large excess of water, and it will be greatest when the material is wetted from a thoroughly dry state. It is expressed in calories per gram of the dry weight of the material. Determinations were made on the four test fibers in an oven dry condition and also after conditioning in atmospheres of higher relative humidity.

The calorimeter used for determination of the heats of wetting was developed at the National Bureau of Standards for measuring the heat of solution of cement and is described in detail in a paper by Newman and Wells [1]. Briefly, the calorimeter was filled with water at 25°C and the weighed specimen, in a water-tight container, was immersed in the water. A resistance thermometer was inserted to indicate the temperature of the water, which was agitated by a motor-driven stirrer. After assembly, the calorimeter was placed in a constant temperature bath controlled automatically at 25°C. When the rate of temperature rise of the water, caused by stirring and thermal adjustment, had reached a constant value, the specimen was expelled quickly into the water (by suitable means) and the resulting temperature rise noted. The heat evolved was calculated from the rise in temperature and the heat capacity of the calorimeter contents.

For the comparative measurements with which this study was concerned, the heat capacity of the calorimeter contents was calculated rather than precisely measured. The water was weighed and the heat capacity obtained from the weight and the known specific heat, while a constant estimated value was assigned for the other contents of the calorimeter (specimen container, supports, stirrer, etc.).

In all cases the fibers were cut into short lengths (mostly about 1/8-1/4 inch) for these determinations and the cut material was dried in a circulating-air oven at 100-105°C for at least four hours. For the determinations of heat of wetting from the dry state, the sample container was filled directly from the oven and cooled in a desiccator before weighing. Inasmuch as most fibers exhibit hysteresis, the material conditioned to higher moisture contents was also oven-dried first so that equilibrium would be approached from the same direction in all

instances. Two conditioning rooms were available, one maintained at 73 ± 2°F and 50 ± 5% relative humidity, the other at 72 ± 2°F and 65 ± 2% relative humidity, and the fiber specimens were conditioned three days or longer before test. The moisture regain (weight percent of moisture present, based on the dry weight of the material) was calculated from the weight increase during conditioning. At least two determinations were made at each condition and the average values obtained are given in Table 1. Published values for the heats of wetting from the dry state of cotton, wool, and jute are 11.0, 26.9, and 18.2 cal/g, respectively.

Table 1. Heats of Wetting of Cordage Fibers

	Conditioning				
	oven dry	50% RH		65% RH	
Fiber type	ht. of wetting	moist. regain	ht. of wetting	moist. regain	ht. of wetting
	cal/g	%	cal/g	%	cal/g
Abaca, C. A. Light	12.1	8.0	4.6	10.7	3.3
Abaca, Davao	12.2	8.2	4.4	10.4	3.3
Abaca, non-Davao	13.0	8.3	5.0	10.2	3.3
Sisal, Haitian dry	16.4	8.4	5.6	10.6	4.2

4. Self-Heating Measurements

The apparatus and method used for the self-heating studies and analysis of the data obtained have been previously described [2,3]. Thermocouples were placed within a cylindrical specimen 2 in. in diameter by 2 in. high. The specimen was prepared by spiral winding of fiber bundles of appropriate length and approximately 1/2 in. diameter into pancake discs 2 in. in diameter. Several discs were stacked to make an overall height of 2 inches. The assembled specimen was then placed in an open wire basket or a stainless steel beaker and mounted within the furnace designed for the self-heating measurements. Two tests for each material were performed in order to establish satisfactory reproducibility between duplicate tests.

From an initial temperature setting of 150°C, all of the cordage fibers tested indicated self-heating properties which led to eventual ignition. The time required for the samples to reach a pre-set furnace

cut-off temperature of 280°C are listed as follows:

Abaca, C. A. Light -- 12 hours
Abaca, Davao -- 9 hours
Abaca, non-Davao -- 11 hours
Dry Haitian sisal -- 17 hours

From the above it is seen that of the four materials Davao required the shortest time to ignition.

The slope of the time-temperature curve at several temperatures was plotted against reciprocal absolute temperature and results are shown for one test on each material in Figure 1. A straight line has been drawn through these points and the activation energy "E" determined from its slope. Comparative rates of self-heating at any temperature may be read directly from the graph; for example, at 190°C ($1/T = .00216°K^{-1}$) the dry Haitian sisal exhibited self-heating at a rate of 0.175 deg C/min. The values of the kinetic constants determined from the lines in Figure 1 are listed in Table 2 for the applicable temperature ranges. Although all specimens were conditioned in an atmosphere maintained at 73 ± 2°F and 50 ± 5% relative humidity prior to test, the kinetic properties are considered typical of dry materials because of the elevated temperatures of test.

Table 2. Physical and Kinetic Properties

Material	Temp. Range °C	Density* ρ g/cm^3	Specific* Heat c cal/g °C	Thermal* Conductivity k cal/sec cm°C	Activation Energy E kcal/mole	Heat Generation Coeff. A $cal/sec\ cm^3$
Abaca, C. A. Light	150-250	0.64	0.32	.00041	26.7	2.48×10^{11}
Abaca, Davao	150-250	0.64	0.32	.00041	27.2	6.55×10^{11}
Abaca, non-Davao	150-250	0.64	0.32	.00041	25.8	1.02×10^{11}
Haitian Dry sisal	150-250	0.64	0.32	.00041	25.7	4.89×10^{10}

* Values assumed to be typical for stored bales.

Thermal conductivity and specific heat measurements were not made for each of the materials. However, if the assumption is made that a typical bale of cordage fiber material would have a density of 40 pcf (.64 gm/cm^3) the values for thermal conductivity and specific heat would approximate those of wood which at this density would have values of 0.1 Btu hr^{-1} ft^{-1} °F^{-1} (4.13 x 10^{-4} cal sec^{-1} cm^{-1} °C^{-1}) and .32 cal g^{-1} °C^{-1}, respectively.

5. Calculation of Critical Size

In order to estimate the critical size for ignition of a mass of self-heating material, the analysis presented by Enig, Shanks and Southworth [4] was used. This related the half-thickness of a material of given thermal and kinetic properties with the temperatures at the center and the surface, under critical steady-state conditions.

The assumption was made that the kinetic properties measured over higher temperature ranges may be applied to the temperature range of practical interest for ordinary storage (20-100°C) and it was further assumed that the thermal properties would apply over the whole temperature range. Determinations of the critical diameter for a sphere, and the critical thickness for a slab with lateral dimensions large compared to thickness, have been made for each material and are listed in Table 3 and shown graphically in Figure 2.

6. Additional Exploratory Tests

Again assuming the specific heat of 0.32 cal/g °C to be typical for stored bales of the fibers, the values determined for the heats of wetting of the fibers would correspond to temperature increases ranging from 10-50 degrees C. In actual storage the most serious situation, that of completely dry fibers becoming completely wetted, would not be likely to occur, and hence the greater increases within that range could not be expected to result from wetting alone. The stored fibers might well have a moisture content similar to that resulting from the conditioning at 50 percent relative humidity, however, and temperature increases of around 15 degrees C would appear quite possible from a heavy wetting of the storage.

Several tests were performed in an effort to examine briefly the combined effects of the heat of wetting and chemical kinetic self-heating. Because of the drastic cooling effect of liquid water on a self-heating specimen, the adiabatic furnace test was arranged so that

Table 3. Critical Size Calculations

Material	Critical Diameter of Sphere for Surface Temperature of			Critical Thickness of Slab* for Surface Temperature of		
	20°C (68°F)	50°C (122°F)	100°C (212°F)	20°C (68°F)	50°C (122°F)	100°C (212°F)
Abaca, C. A. Light	112 ft	14.7 ft	1.0 ft	58 ft	7.6 ft	0.5 ft
Abaca, Davao	112	13.4	0.9	58	6.9	0.5
Abaca, non-Davao	84	12.4	0.9	43	6.5	0.5
Sisal, Haitian dry	111	15.7	1.2	58	8.1	0.6

* Lateral dimensions assumed large compared to thickness.

steam could be introduced into the test specimen through a perforated teflon tube embedded about midway between the center and outside of the specimen. When steam amounting to approximately 25 percent of the weight of the specimen was supplied, with the specimen temperature at about 150°C, temperature increases ranging up to 17 degrees C resulted. When the steam was introduced at an initial sample temperature of 96°C, the temperature rose to 126°C. These increases are in accord with those suggested by the heat of wetting data, and it would appear that, under some conditions, they might be sufficient to raise the temperature of a large storage pile to the critical point from which self-heating to ignition could proceed.

In addition to the above tests, differential thermal analyses were made on two of the fibers, the Davao abaca and the Haitian sisal. In this analysis, which compares the heating behavior of a test material with that of an inert material, specimens of the two materials are placed in the same furnace, which is then heated at a given rate. Automatic recording equipment provides a continuous record of the difference in temperature between the two specimens, as indicated by a differential thermocouple, and of the actual temperature of the test material, as indicated by a separate thermocouple. It is assumed that the effect of the furnace heating alone is fairly represented by the temperature of the inert material, and that pronounced differences in the temperatures of the two specimens indicate some change, exothermic or endothermic, in the test material. In Figure 3, the temperature difference between the inert and the test material is plotted against the actual temperature of the test material.

The two fibers showed a generally similar behavior, but the changes differed notably in degree. Thus, the endothermic reaction, (likely the production of gaseous degradation products) which became predominant at around 300°C in both cases, was decidedly more pronounced for the sisal than for the Davao abaca. This difference in heat absorption is probably related to the longer time required for the sisal to heat to ignition, which was noted in the self-heating determinations. The differential thermal analyses indicate further that ignition resulted in a more rapid evolution of heat above 400°C from the sisal than from the Davao abaca.

7. Conclusions

Measurements of the heats of wetting and the self-heating properties of four cordage fiber materials have been made. All materials showed self-heating over the temperature range of 150-250°C with slight

differences among the fibers. Activation energy values ranged from 25.7 to 27.2 kcal/mole, values typical of fibrous wood products.

From the kinetic data, critical size calculations have been made for surface temperatures ranging from 20-100°C. The critical thickness values calculated for normal storage temperatures of 20-30°C (68-86°F) are sufficiently high that any usual type of storage of the dry fibers at those temperatures would appear to present no hazard of self-ignition. Should the storage temperature exceed that range significantly, however, and approach perhaps 50°C (122°F), the data clearly suggest that the specification of a permissible pile size would be advisable.

Prolonged exposure to elevated ambient temperatures will, of course, raise the temperature of stored fibers to some extent. The temperature may also be increased if the fibers become wetted, the extent of the increase depending on the original condition of the fibers, the degree of wetting, and the various conditions of storage. The data obtained indicate that, under some conditions, an increase of 15 or more degrees C might result from wetting the fibers. Such an increase could produce a temperature from which, under favorable conditions, self-heating to ignition would appear possible in large storage piles.

These experiments and the calculations which have been made indicate that definite precautions would be advisable for fiber storage which may be subject to elevated ambient temperatures or to wetting. It should be noted, however, that the calculations are based on assumed thermal properties which may be considerably different from the actual properties of the baled fibers. The density was assumed to be 40 pcf, based upon the reported bale size of approximately 2 by 2 by 4 ft and a weight of approximately 650-700 lb. A thermal conductivity value of 0.1 Btu/hr ft °F, representative of wood of similar density, was arbitrarily assigned. Although critical pile size is a (square-root) function of the ratio of thermal conductivity to density (which are roughly proportional to each other), it may be noted that a 50% increase in thermal conductivity at the same density (or a corresponding 50% decrease in density at the same thermal conductivity) would result in a 25% increase in calculated critical size at all temperatures. Finally, it must be emphasized that calculation of critical size for ignition is based upon the very broad assumption that kinetic properties measured at elevated temperatures apply at the lower temperatures. In some cases, the simple theory for thermal ignition assuming a single reaction with no loss of reactant may be inadequate to permit extrapolation to normal storage temperatures.

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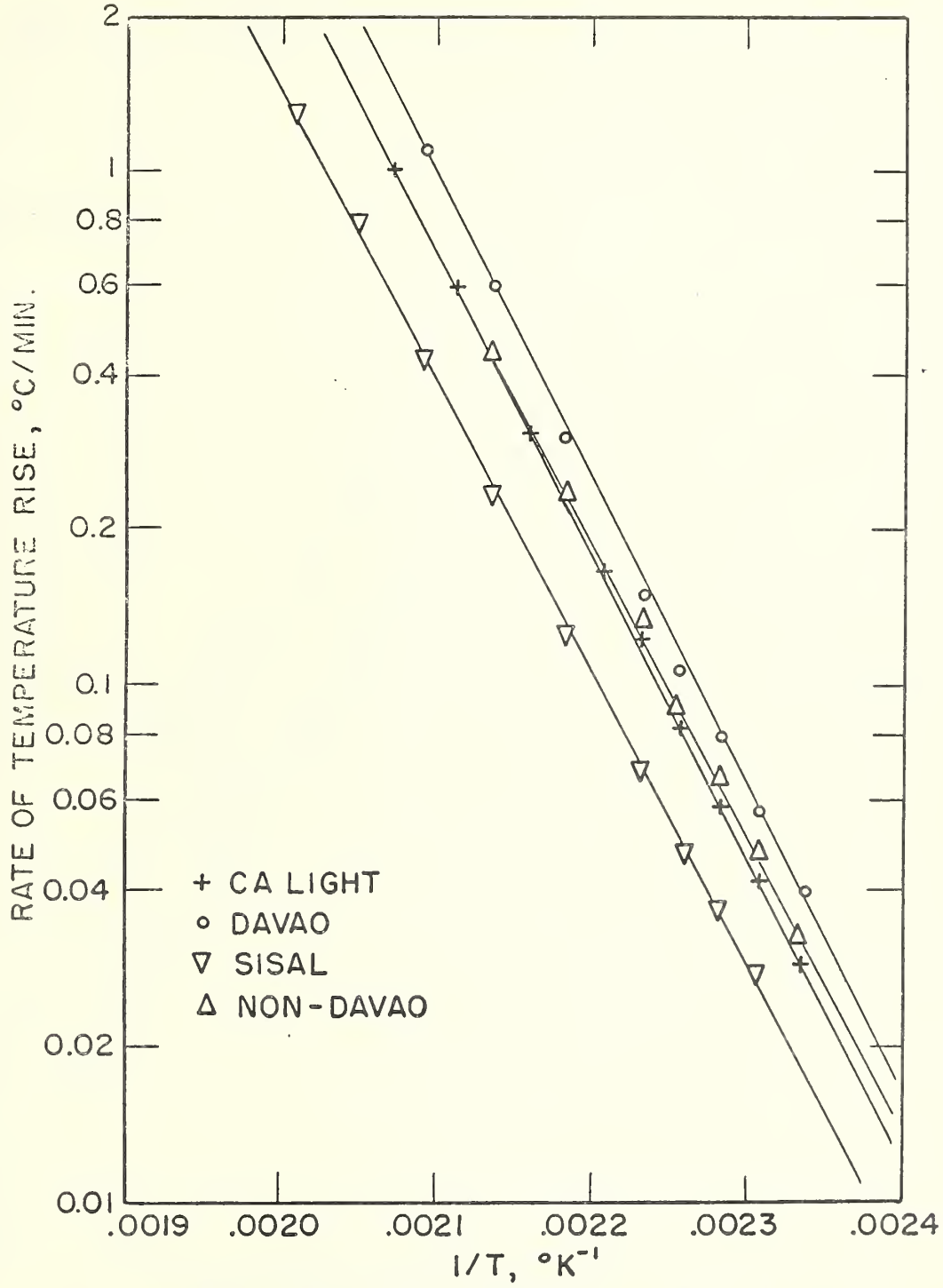

FIG. 1—ADIABATIC SELF-HEATING DATA ON FOUR CORDAGE FIBERS

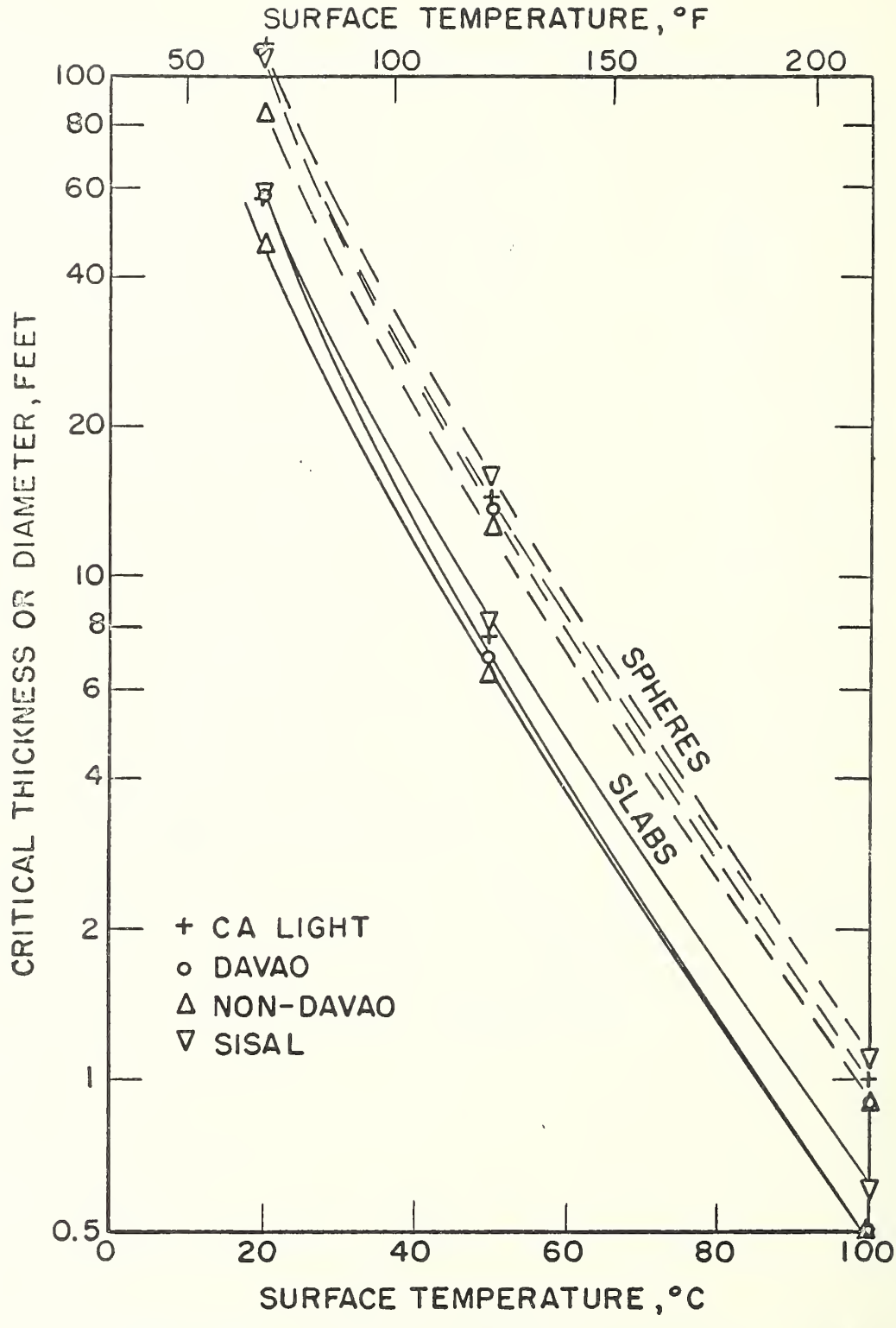

FIG. 2—COMPUTED CRITICAL DIMENSION AND SURFACE TEMPERATURE FOR FOUR CORDAGE FIBERS

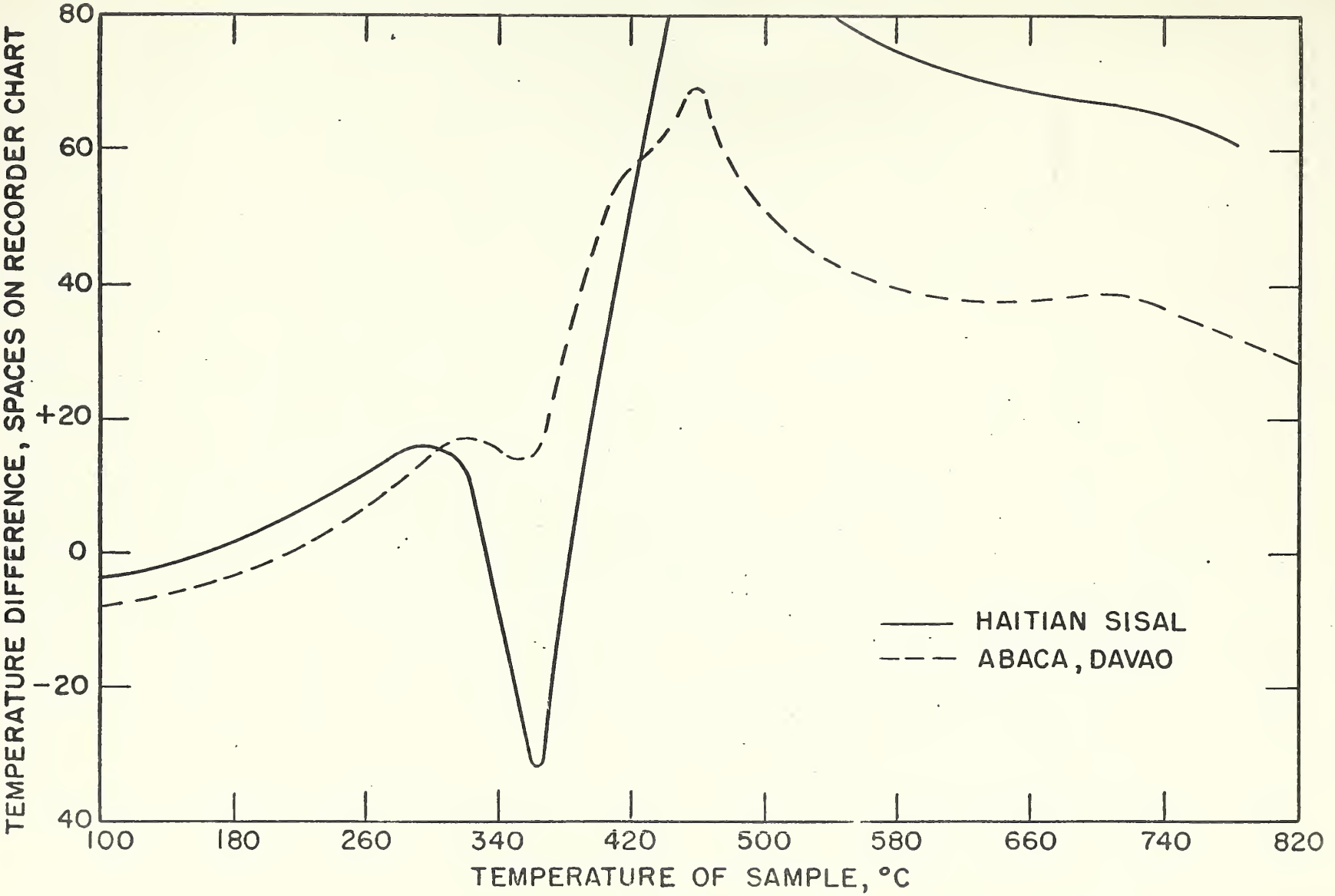

FIG. 3 – DIFFERENTIAL THERMAL ANALYSES ON TWO CORDAGE FIBERS


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