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**The Effect of Drying Conditions
on the Surface Strength of Clay
Coated Paper**

A Thesis

Submitted to the Faculty

Department of Paper Technology

School of Applied Arts and Sciences

Western Michigan University

**... in Partial Fulfillment of the
Requirement for the Degree of Bachelor
of Science**

by

Lawrence A. Gaspar

September 25, 1962

Abstract

The importance of the continuous-film forming properties of the polymer via fusion upon heating is second to none. Yasuda states that it depends on the probability of two particles coalescing upon the application of heat versus the acceleration of the rate of removal of the disperse medium from the coating. Naturally it would seem that excessive rates of drying would not permit the adhesive to fuse, but it may also alter the distribution of adhesive throughout the coating in either case. Eames has suggested the effects of certain variables on the distribution of starch in starch-clay coatings, but the fact that starch insolubilization in coating formulations has proved rather difficult may influence its redistribution pattern upon drying.

From a theoretical standpoint the basic difference, the thermodynamic nature of the synthetic latex compared to the starch, may account for its difference in behavior in coatings applied on paper, especially when they are dried. One particular property of a latex which might reflect the latter is the "tackiness" of this type of adhesive.

Koller has suggested that the exposed part of the polymer molecule on the surface, not specifically bonded, may transfer forces to the coating wherein they are distributed. This may account for its stability in a coating to some types of energy.

For a rational approach to the evaluation of evidence which may be present, one must recall the diverse nature of paper, its varying properties, and the effect or influence of these taken as a totality or individually.

The Effect of Drying Conditions on the
Surface Strength of Clay Coated Paper

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I. Introduction

A. Statement of Problem

Past experiment has substantiated the belief that the water in a moist sheet of paper evaporates from the moist surface into the space beyond, and also flows toward the hotter drying surface on a hot surface dryer. The vaporized water at the hot surface dryer escapes from the sheet to the exterior of the sheet and into the region beyond.

The purpose of this thesis is to investigate the surface strength characteristics of coated paper dried at varying temperatures under similar conditions. It is suggested that the slower removal of water may enable better surface bonds to form between the coating and the substrate, and in the coating.

A coated sheet of paper dried at a slower rate will, perhaps, have better surface strength characteristics than a coated sheet dried at a faster rate. The slower drying rate may permit the coating color to enter the voids of the substrate and form more effective bonds. A better bonding strength may then develop.

B. The Structure of Clay Coatings

1. Structure and Nature of Clay Particles

Recent discoveries (1) have shown that there is a highly significant correlation between the orderliness of the configuration of the atoms within the kaolinite¹ structure and corresponding perfection of the geometry of its crystal particles. Stated in perhaps oversimplified form, when the component atomic sheets in the structure are stacked in orderly fashion, one upon the other, then the crystal plates of the kaolinite will ordinarily appear as clean-cut geometric hexagons.

Furthermore, when atoms in the structure are well ordered and the kaolinite plates are well crystallized, the resulting kaolins will be of low viscosity.

1. The term "kaolinite" is used when speaking of a crystal, or a group of particles, of the (comparatively) pure mineral. The term "kaolin" is used in reference to the mineral as it may be found in a kaolin deposit containing, perhaps, silica, mica, and/or other accessory minerals.

The pH of papermaking clays in the natural state is usually slightly lower than neutral although it does range from 7.2 down to 3.8 and frequently reflects the presence of accessory non-clay chemical residues. Coating clays which have been chemically decolorized usually show pH values ranging from 3.5 to 5.5 except in the case of so-called "predispersed" grades to which alkaline deflocculators have been added after processing.

One of the most important recent discoveries contributing to a rational understanding of how kaolinite clays function as coating pigments, is the fact that they change their generic particle shape at about 2 μ e.s.d. (estimated spherical diameter). Finer than 2 μ , the kaolin particles are predominantly hexagonal plates. They may occur as single individual crystals or they may consist of very small and anisometric aggregates of such hexagonal plates.

These aggregations are much more nearly isometric in shape than are the single plate particles.

When the crystalline plates of clay are applied to a paper web in the form of a coating color, they assume the common, characteristic orientation parallel to the substrate upon which they are placed. For a kaolinite whose particles are larger than 2 μ (e.s.d.) the laminated stack formation of crystalline plates is predominant, whereas the single plate shape is a characteristic of those kaolin particles finer than 2 μ dimension.

2. The Nature of Adhesives Used in Clay Coatings

Natural adhesives, such as casein, animal glue, starches, and proteins, are the most widely used today. Economically their importance to industry is primary. However, certain properties of a coated paper cannot be obtained with the same quality as with synthetic binders.

Latices, in general, will improve flexibility, smoothness, gloss, and printing quality of coated papers. These property modifications are generally attributed to the inherent and the thermoplastic nature of the adhesive.

However, some latices may be unstable to mechanical action, and they are tacky. Another disadvantage, after using all latex binders for coated papers, is that the difficult redispersion of the lattice particles permits very little reclamation of the raw stock for reuse.

Casey (2) suggests that the adhesive exerts a profound influence on the properties of the coating mixture and the properties of the final coated paper. The functions of the adhesive in pigment coating are as follows: (a) to serve as a carrier for the pigment, (b) to impart the required flow (rheological) behavior and water (and adhesive) retention to the coating mixture, (c) to bond the pigment particles together in the dried coating and to bond the pigment to the body stock.

3. The Distribution of the Adhesive in the Coating

According to Dappen (3) the mechanism of starch distribution (clay-starch coatings) is thought to involve primarily capillary competition for the vehicle between the substrate and the coating, but is also influenced by the drying forces. Drying with a hot air blast on the coating side was found to increase the ratio of starch to clay in coatings on paper continuously from the fiber to the air interface.

Eames (4) suggests that the major loss of adhesive to the substrate occurs in the saturated state of flow and that low rates of penetration of vehicle favor the maintenance of this type of flow, even to the extent that a greater volume of vehicle penetrates a substrate of small pore size than it does a substrate of large pore size.

With these suggested adhesive distribution mechanisms during drying the rheological flow-behavior of latex-pigment coating colors and the thermoplastic nature of the adhesive should be kept in mind. Upon heating the fusion of tacky adhesive particles would probably alter the adhesive distribution.

It would seem that a more viscous adhesive would distribute itself or remain in the coating to a greater extent than in the raw stock through

penetration, because of greater fluid friction forces operating.

McLaughlin and Schucker (5) have reported that emulsion polymers do not appreciably penetrate the substrate.

Eames reported that coatings (clay-starch) tended to lose more starch to the substrate with decreasing pore-size of the substrate. The thinner but more concentrated layer of starch found in smaller pore-size substrates may contribute to pick strength by strengthening the substrate-coating bond and the layer of the substrate, was suggested by Eames as an explanation that Casey and Libby did not find a correlation between depth of adhesive penetration into the bodystock, and wax pick strength for starch-clay coatings on paper.

C. The Drying of Coated Paper

Three modes of heat transfer, namely, conduction, convection, and radiation are recognized. Radiation heat can be transferred without a medium in a form of electromagnetic wave motion, while convection uses a fluid as the medium, and conduction involves transmission of heat through an opaque solid.

Conduction and convection drying both occur during the drying cycle of a hot surface dryer. Air of low moisture content and high temperature directed toward the surface of the coating is a good method for drying by convection. The impinging air stream directed toward the surface of the coating should be of sufficient velocity and quantity to penetrate the moisture vapor and air film immediately above the coating surface.

A hot surface dryer uses conduction predominantly because the heat transferred from the hot surface is the main driving force and source of energy for the removal of the moisture from the coated sheet. The rate of drying and drying capacity will be influenced by the temperature of the air supply, the moisture content of the air supply, and the intimate contact of the air supply with the coating surface.

If these are maintained constant, then the drying will vary with the heat energy transferred by the hot surface dryer.

Dreshfield(6) reported that water in a multi-ply assembly of paper sheets dried with a hot surface dryer evaporated from the exterior of the sheets into the air. The maximum moisture content was located 20 to 30% of the distance from the open to the hot surface. Liquid water which was initially between this zone and the hot surface moved toward the hot surface; liquid water which was between this zone and the cooler surface moved toward the cooler surface. The movement of liquid water was in a direction of a decreasing moisture content and was predominantly toward the hot surface of the sheet. This phenomena showed that the water vaporized at the hot surface, condensed, giving up heat, which was conducted to the water in the maximum moisture content zone for evaporation from the cooler surface.

Sometime during the falling-rate period the driving force for the evaporation of water from the zone of maximum moisture content was heat conduction from the hot surface. This heat transfer continued until the multi-ply sheet was dry.

II. Historical Review

Styrene-butadiene copolymer latices containing about 60% of styrene were pioneered by the Dow Chemical Company (7). Early patents covering this application were obtained by the S.D. Warren Company. In recent years other polymers have been developed for this use; in particular the acrylates and acrylate copolymers have found extensive use for the on-machine coating of paperboard and for breadwrapping papers. In England butadiene methylmethacrylate copolymer latices have been used successfully, whereas in Germany the acrylate-vinyl acetate copolymers have gained wide acceptance. In the United States of America polyvinyl acetate polymers and copolymers are also under intensive development.

Traditional papers have followed the literature review chronologically. Since a small amount of information has been reported, this paper will include topics which seem related to the subject in a somewhat remote fashion.

According to the suggestion of R.M.K. Cobb (8) the adhesive demand depends on the percent of available voids in the coating color, and is entirely independent of the specific surface and pigment particle size. Naturally it is important to bear in mind adhesive demand concepts, but more so to recall factors which affect the coating strength.

Eames (4) reported that the Transverse Tensile Strength (TTS) of clay-starch coatings on porous substrates increase with:

1. decreasing pigment particle size
2. increasing substrate pore-size
3. increasing adhesive content
4. lower rates of drying.

Void volume distribution, stress concentrations, residual stresses, and particle alignment are believed to affect the distribution of TTS within a pigment coating; but their relative contributions to TTS are thought to be subordinate to, or dependent on, the adhesive distribution.

Kraske (9), about clay-starch coatings, reports that the unbonded surface area of these coatings increases substantially as the particle size of the clay used in the coating is decreased.

Kraske also suggests that the relatively poor orientation of the large clay particle fraction coating conceivably could result from the rapid flow of vehicle from the interparticle spaces which should exist in this coating during the vehicle migration stage of drying . If this were the case, the particles would not have time to align themselves in the plane of the raw-stock before they were "immobilized." The comparatively large mass of these particles would offer additional resistance to alignment by fluid friction forces operative during the vehicle migration stage.

Avery, Sinclair, and Guy (10) suggest that the ability of a copolymer latex, seemingly, to bind itself to pigment would be relatable to its ability to form a continuous film by fusion upon drying.

A belief that the unabsorbed portion of the chain molecule (polymer) projecting from the absorbed layer, transfers forces into the adhesive layer when exposed to tensile or sheer stress, is advocated by Koller (11).

Meloran (12) states that the adhesion of high polymers to cellulose is a function of several variables:

1. the tack temperature, dielectric constants of the polymer, and dipole moments of polymer polar constituents
2. the nature of the polar groups within the polymer and the modified cellulose
3. and the close relationship of the adhesion temperature to the adsorption and cohesive energy.

According to Yasuda and Stannett (13) the properties of clay-coated papers depend on many variables; included among them is drying conditions. About clay-coated papers dried in an air-circulating, they report that:

1. If the distribution of polymer is changed, it affects chiefly the binding strength or the varnish holdout of the coated papers.

2. A vinyl acetate homopolymer latex gives greatly improved binding strength at higher drying temperatures, due to better film-forming properties of this polymer at higher temperatures (glass transition temperature = 28° Centigrade).
3. The gloss was affected with increased drying temperature. These results undoubtedly reflect the changes in the surface contours of the coating as the latex has more opportunity to fuse and flow.
4. The drying temperature exerts two main effects which compete with each other, (a) heat fusing and (b) acceleration of the rate of water removal from the system, which may cause excess penetration of the adhesive into the paper substrate or uneven distribution of the adhesive in the coated paper. They mention that part(b) varies with the probability of the polymer particles coming into contact with each other.

III. Analysis of the Problem

A. General

Hot surface drying with a high temperature will result in the rapid removal of water from the coating color with the proper drying conditions of air supply. Immediately after the coating color has been applied to the substrate, absorption of the water by the raw stock will tend to reduce the mobilization of the adhesive and clay particles. Fluid friction forces and the tackiness of the adhesive, which is influenced by the drying temperature, will further immobilize the coating. Flow of the coating into the voids of the raw stock with the high temperature surface dryer may be at a minimum; and Dappen (3) reported that the adhesive content in clay-starch coatings, dried with a hot air blast directed at the coating surface, increased as the distance from the fiber to the air-coating interface decreased.

These considerations suggest that the lower temperature surface may improve the strength of the coating and the coating-raw stock interface. Fusion of the adhesive will occur more slowly at a lower temperature. The resulting bond formations may be more uniform and less subject to stress concentrations set up by the more rapid drying.

B. An Outlined Approach for Solving the Problem

1. The main variable to be studied is the drying temperature effect on the strength properties.
2. The raw stock, coating color, and drying technique and apparatus shall remain the same for each individual sheet that is coated.
3. All samples made at approximately the same time, should be tested during a time interval of twenty-four hours for each individual test. This is critical because test values for a single specimen may vary with time.

C. The Experimental Program — in Outline Form

1. Prepare the coating color as follows:

- a. Disperse the clay² at 65% solids in a Day Mixer.
 - b. Cook the casein (use ammonia and borax as cutting agents).
 - c. Stabilize the latex (Rhoplex B-15) with a small amount of cooked casein.
 - d. Slowly mix the casein and then the latex with the clay dispersion with constant stirring. Allow the contents of the mixer to become uniform.
2. Prepare the raw stock for coating (condition³ the sheets).
 3. Measure the viscosity of the coating with a Brookfield viscosimeter.
 4. Use the drawdown method and coat on the wire side of the raw stock in the machine direction on a specified sheet size by means of a wire wound rod.
 5. Immediately dry the sheet on the special drying apparatus with a drying technique to be described later.
 6. Condition the sheets, and then determine the coating weight per ream (500 - 25 x 38).
 7. Super calender the sheets.
 8. Evaluate the test specimens according to the I.G.T. dynamic pick, brightness, opacity, gloss, smoothness, caliper, and Vanceometer oil penetration test results.

Measurement of Surface Strength by the I.G.T. Print and Pick Tester

One of the more important parts of this study is the measurement of the surface strength of the supercalendered, coated sheets. Two researchers have made a study of the testing machine and its results.

Hemstock and Swanson (12) have reported the belief that variations in the

2. An Edgar clay, Spray Satin, manufactured by Minerals and Chemicals Philipp Corporation, was used.

3. Condition is a term which means a time lapse of at least 24 hours during which the test specimens are kept in an atmosphere of $50 \pm 2\%$ relative humidity and $73 \pm 2^{\circ}$ F.

roughness of the coated sheets are responsible for much of the difficulty in reproducing the test. Then correlations that have previously been reported between particle size of the pigment and the pigment adhesive demand must, therefore, be explained on the basis of differences in the effectiveness of the pigment particles in plugging the surface pores of the raw stock.

Physical factors usually considered are:

1. the intimacy of surface contact between adhesive and adherend
2. the surface area of contact
3. the stress conditions of the bond.

In clay-adhesive systems a number of factors influence the intimacy of contact between adhesive and adherend:

1. Water is always present so that clay is probably bonded to the fibers somewhat as follows: clay-water-adhesive-water-fibers.
2. It has been demonstrated that clay particles in water are negatively charged so that, depending upon the salt content and exchangeable ions present, a potential energy barrier exists around each clay particle. It is reasonable, therefore, to expect that the intimacy of contact between clay and adhesive is dependent upon the properties of the intermicellar solution, and that air bubbles will decrease bond area due to less intimate contact.

The cause of adhesive-adherend failure can be attributed to the stress conditions of the bond during and after its formation. Residual stresses may be set up by:

1. A dimensional change in the system during drying
2. Differences between the coefficients of thermal of adhesive and adherend
3. Differences between the stress-strain characteristics of adhesive and adherend.

In summary , Hemstock and Swanson have mentioned that variations in backing

and specimen roughness probably provide one of the greatest sources of error in this method. Also coating flow into voids and only oil contact with the coating peaks are sources of error.

IV. Experimental Equipment and Techniques

A. Coating Color Preparation

Five pounds of air dry clay were dispersed at 65% solids with calgon (0.3% based on the weight of clay) in the Day Mixer for 20 minutes. Casein was wetted out with the water it was cooked with for 20 minutes. Ammonia and borax were added and the 15% solids mixture was cooked for 20 minutes at $65 \pm 3^{\circ}$ C. in a double boiler. The cooked casein was rapidly cooled to room temperature.

The cooled casein was added to the Day Mixer slowly and allowed to distribute itself throughout the dispersed clay for 20 minutes. This prevented the so-called "casein shock" or pigment flocculation. The Rhoplex B-15 was taken from its container and put into the pan which had contained the casein, and the remaining dilution water was added to this pan. What little casein that remained in the pan may have helped to stabilize the emulsion.

The diluted emulsion was then added to the Day Mixer and mixed for 30 minutes to make the total mixing time for the coating color equal to 70 minutes.

The viscosity of the coating color was determined with a Brookfield viscosimeter and the total solids of the coating color calculated to be 53%. The visible uniformity and relatively high fluidity of the coating color did not necessitate the screening of any lumps, which were at a minimum.

Components of the coating color and the results of the viscosity measurements are listed in the following tables.

Table I. Components of the Coating Color Parts by Weight

Water	50
Clay	50
Calgon	0.3 based on the weight of clay
Casein	4.0 based on the weight of clay
Rhoplex B-15	8.0 based on the weight of clay
Ammonia	4.5 based on the weight of casein
Borax	0.5 based on the weight of casein

Table II. Viscosity of the Coating Color (Temperature = 28° C.).

<u>Spindle number on Brook-</u> <u>field viscosimeter</u>	<u>Revolutions</u> <u>per minute</u>	<u>Viscosity in centipoises</u>
1	6	136
1	12	117
1	30	110
1	60	104
2	60	128

B. Preparation and Properties of the Base Stock*

Thin cardboard segments (8x0.5 inches) were stapled to the raw stock samples across their width perpendicular to the machine direction on the wire side. These provided a means of grasping the wet coated sheet and holding it against the surface of the drum dryer, and maintaining good contact with the surface of the dryer. Then the raw stock was conditioned for 24 hours prior to coating.

Traditionally, raw stocks used in coating experiments are diverse in nature. The raw stock used in the program contained 85% deinked fiber and approximately 6-8% filler clay. Following are other properties of the raw stock which may be of interest.

Table III. Properties of the Base Stock

General Electric Brightness	74%
Bausch and Lomb Opacity	85%
Caliper (mils)	4.1
Porosity (seconds)	33
Bekk Smoothness (seconds)	1.3
Photovolt Gloss	6.0%
Easis Weight (25x40-500)	46 pounds
Burst Factor	0.37 points per pound
	<u>Machine Direction</u> <u>Cross Direction</u>
Tear (grams of force)	51 88
Breaking Length (yards)	14,600 7400
Fold (double folds)	22 12
Vanceometer Oil Penetration**.. the initial and final reading equals	
14 microamperes, the ten second reading equals 16 microamperes.	

*.H. R. Hall of Allied Paper Corporation generously donated the raw stock.

**..All tests other than the Vanceometer Oil Penetration test were carried out according to Tappi Standards.

C. Method of Coating

The coating color was made the day before. Noticeable evidence of color, odor, or viscosity change did not occur, and therefore it is probable that the coating color did not spoil during the time it was used.

The prepared raw stock was placed on a stack (one-half inch thick) of soft paper. A portion of the coating color was quickly poured across the paper width on the wire side. A number 15 Mayer rod was then used to distribute the coating uniformly over the raw stock surface in the machine direction. The coating weight was equal to 15.0 pounds on an air dry basis per ream(25x40-500).

D. Drying Apparatus and Methods

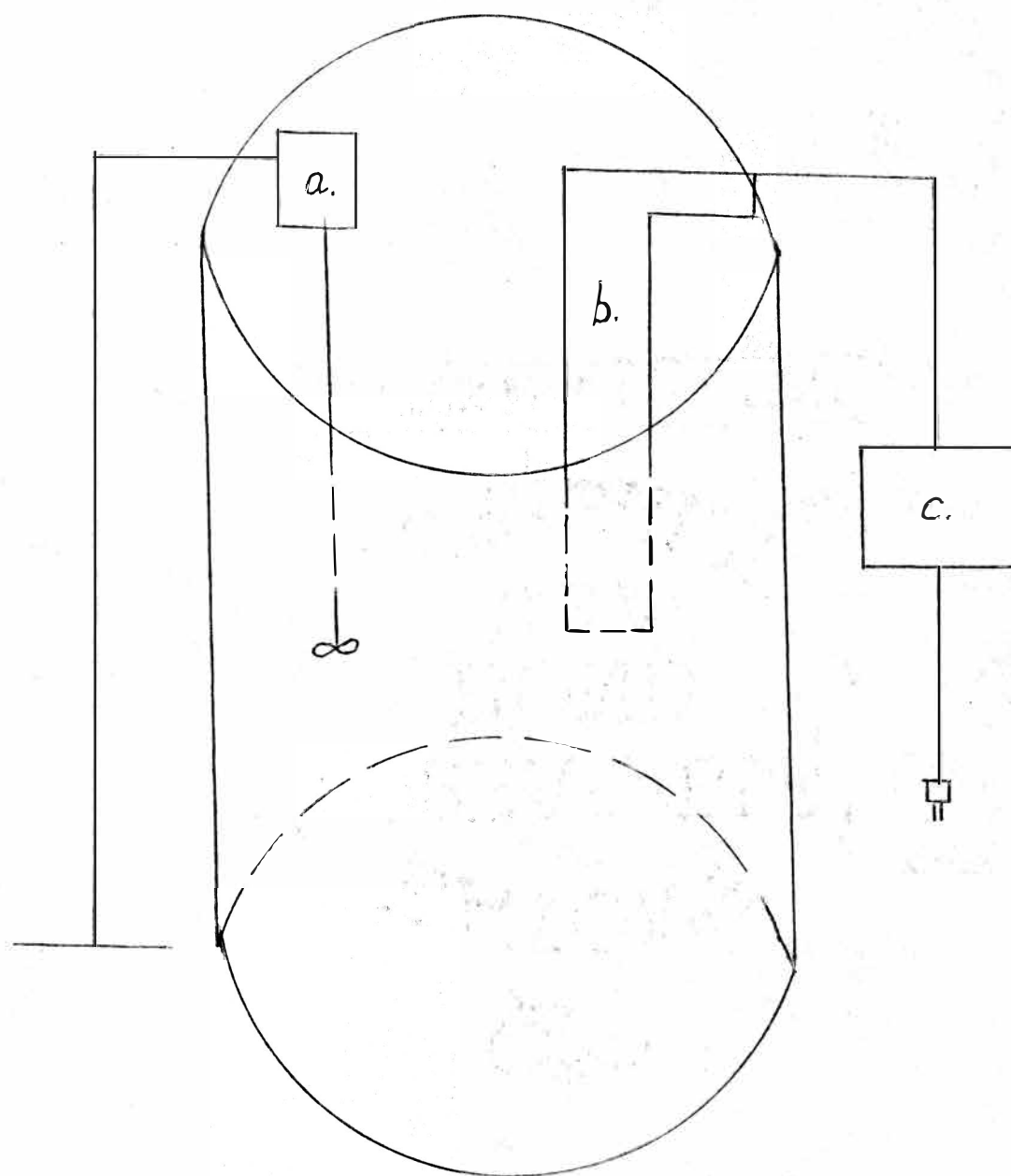
The first part of the drying apparatus consisted of a cylindrical metal can (diameter = 18 inches, height = 24 inches) which contained water as a heating medium. A mechanical stirrer and 1000 watt immersion heater were inserted into the can (see figure I.). A steam coil was used for preliminary heating.

The other part of the apparatus was an oven which was regulated at the same temperature as the surface dryer. A voltage regulator permitted rigid control of the rate of heating in the cylindrical, while a thermostat control enabled regulation of the oven temperature.

Total drying time for each sheet was four minutes. It is understood that the time required for drying at the hotter temperature may be less. However this time was selected for uniformity. The coated sheets were initially dried on the surface dryer by placing them against the dryer surface and maintaining tension by grasping the thin cardboard segments at each end of the coated sheet and holding the sheet against the dryer. These were quickly put into the oven at the same temperature for the remaining drying time. At each temperature (90, 70, and 50° C.) coated sheets were dried for 4, 2, 1, 0.5, and zero minutes on the surface dryer. The hot surface contacted the non-coated side of the sheet.

Figure 1. A Diagram of the Surface Dryer

- a. Mechanical stirrer
- b. 1000 watt immersion heater
- c. Voltage regulator



E. Supercalendering and Conditioning of the Coated Sheets

The dried, coated sheets were trimmed and allowed to condition. Then they were supercalendered in a constant humidity room (73° F. and 50% R.H.) on a laboratory supercalender. Each sheet was passed through a single nip three times in the machine direction of the sheet. The coated side was next to the metal roll each time. Nip pressure was equal to 4700 pounds per lineal inch. Coated sheets that were tested were selected from those which contained no defects from calendering and were uniform in appearance.

F. Method for Analyzing the Ink-Picked Portion of the Coated Sheet From the
I.G.T. Pick and Print Tester

Samples of the supercalendered, coated sheets dried at each temperature were tested on the I.C.T. tester. The portion picked from the coated sheet by the ink was saved, so that relative differences in the depth of the pick could be determined.

A 0.100 gram sample was extracted with toluene in a tared porous crucible with a gooch suction funnel to remove the ink. The extracted sample was dried in an oven at 105° C., cooled, and weighed. This sample was carefully charred and then ignited at 800° C. for a minimum of eight hours. After constant weight was obtained, the ash was determined by difference. The amounts of the various components before ignition were calculated (See appendix.). This completed the experimental program.

V. Experimental Results

A. General

Certain test values for each supercalendered, coated sheet should be expected to be equal. The coating color, coating apparatus and subsequent supercalendering of the coated sheets is the same for each sample. Therefore it is reasonable that the G.E. brightness values range from 77.5-78.0 %, the B. and L. opacity values range from 90-91 %, and the caliper values are practically equal (3.2-3.4 mils).

Supercalendering may have reduced all three of the above test values from those which might have been obtained from the unsupercalendered, coated sheets. However, this operation was necessary to obtain the final gloss and smoothness which is not characteristic of the unfinished sheet. Some modifications of other test values may have occurred, but a compromise is necessary to obtain other desirable properties, such as, printability and print quality.

B. Photovolt Gloss

The gloss measurements (Table IV.) seem to indicate that the reflecting interfaces at the surface of the coating are relatively uniform, even after being dried at different temperatures.

According to the manufacturers of Rhoplex B-15, the highest gloss for a coating can be obtained with a 100 per cent Rhoplex adhesive system. In blends of Rhoplex B-15 with casein, gloss is sacrificed in proportion to the percentage of casein incorporated into the system. The decrease in gloss is, therefore, a direct line function of the casein content. Also in this particular system the gloss is, seemingly, drying-temperature independent.

C. Bekk Smoothness

In this system a correlation between the temperature at which the coated sheet is dried and the smoothness of the supercalendered, coated sheet is suggested by the values reported in Table IV. There are differences in the values reported for varying times on the hot surface dryer at each temperature, but these are relatively small. The tendency for the smoothness to increase

with decreasing drying temperature for the supercalendered, coated sheets can readily be seen from an average value at each temperature:

- a. 90° C. - 24 seconds
- b. 70° C. - 27 seconds
- c. 50° C. - 32 seconds.

There are several reasons which might be responsible for this phenomenon. The first is the possibility that more casein, compared to the Rhoplex B-15, is present at the air coating interface as the temperature of drying is increased. The brittle casein would not flow as much as the Rhoplex B-15 under the pressure and at the temperature of the supercalender.

The partial immobilization of the coating by evaporation and penetration of the water phase would result in a very viscous coating. This will occur more readily as the temperature is increased because the rate of heat transfer would also be increased, thus the casein could move away from its position in the coating toward the raw stock less as the rate of heat transfer is increased.

Eanes (4) reported that the loss of starch adhesive to the substrate will occur most during the saturated state of flow. It is likely that the saturated state of flow will be prolonged the slower the rate of heat transfer to the system.

The second explanation might be associated with the residual strains produced in the system by the higher drying temperature. The ability of the coating to flow and produce a uniform surface would seemingly be related to the rate of heat transfer. At lower rates of heat transfer the coating would be able to flow a longer time and thus produce a more uniform, smoother surface. Kraske (9) has reported that the clay fraction may not have time to align itself in the plane of the raw stock during the vehicle migration stage, if the rate of removal of the water is too fast.

Table IV. Experimental Results

Test sample ¹	Photovolt gloss (per cent)	Bekk smoothness (seconds)	I.G.T. value ²	Vanceometer ³ (10 second readings)							
				0-10-20-30-40-50-80	seconds						
A	46	24	260	58	86	68	64	63	63	63	
B	43	24	270	54	92	90	85	78	70	62	
C	46	23	250	52	85	76	67	61	60	59	
D	46	21	270	56	70	66	64	63	63	62	
E	46	26	290	56	89	82	76	69	65	62	
F	46	27	270	58	84	68	64	64	64	64	
G	47	28	270	53	72	65	62	62	62	62	
H	46	28	290	59	75	70	69	68	68	68	
I	48	26	290	56	82	68	64	64	63	63	
J	46	28	255	62	90	78	73	72	71	71	
K	49	32	260	60	84	74	70	69	69	68	
L	48	35	260	55	80	74	68	66	64	63	
M	46	29	255	60	81	74	70	69	69	68	
N	46	33	250	56	76	66	64	63	62	62	
O	47	32	250	59	90	82	76	75	74	73	

1. Samples A-E were dried at 90° C.. F-J at 70° C., and K-O at 50° C. For each temperature the first sample listed in each series was dried in the oven for 4 minutes, and successive samples for 2, 1, 0.5, and 0 minutes.
2. These values correspond to the velocity in feet per minute of the I.G.T. tester at which picking first occurs. A number 2 (# 2) IPI ink and the "A" spindle at 35 kg. tension were used.
3. Vanceometer readings in microamperes were recorded at various time intervals from 0 to 80 seconds.

D. I.G.T. Test Values

Originally the I.G.T. pick and print tester was to be used as a critical means for evaluating the coated sheets. Evidently, strength differences that can be measured are such that little difference is noticed. An average value of the mean values at each temperature is 263 feet per minute for the velocity at which picking first begins; the deviation from this mean value for each average value at the different temperatures is within five per cent:

- a. 90° C. - 268 feet per minute
- b. 70° C. - 275 feet per minute
- c. 50° C. - 255 feet per minute.

In general, the picked portion from the coated sheet by the I.G.T. pick and print tester apparently contained an amount of fiber which indicated that the pick was below the coating-substrate interface. After viewing considerable test specimens under a microscope, it was concluded that this was the case. However, the question arose whether any relative difference in the amount of fiber picked from the raw stock existed. To find this out an analysis of the picked portion was carried out. After ashing an ink-extracted sample, calculations were made. The results of these trial and error calculations and those for a non-picked coated sheet are:

<u>Drying temperature in degrees Centigrade</u>	<u>Grams of paper per gram of coating in picked portion</u>
90	1.64
70	1.42
50	1.44
.....
non-picked coated sample (5x7 inches)	3.22

A sample calculation may be seen in the appendix.

From this data it is apparent that there is more strike-in of the adhesive into the raw stock at the higher drying temperature compared to

the lower temperature. This is reasonable, as Yasuda and Stannett (13) have suggested that the accelerated rate of removal of water may cause excess penetration of the adhesive. In this case it seems that the adhesive has penetrated farther into the raw stock for those coated sheets dried at 90° C. The presence of more adhesive in the raw stock may permit stronger or more bonds to form in one or more of the following ways:

1. specific adhesion
2. secondary valence forces
3. primary valence forces.

E. Vanceometer Oil Penetration Test

By direct examination of the results from the Vanceometer oil penetration test, there is no visible trend. From figures II-VI it is seen that the oil absorption of the supercalendered, coated sheets seems to be greatest for those coated sheets dried at 90° C. Classic theory accounts for oil penetration according to the amount of void volume contained within the sheet. This indicates that the coated sheets dried at 90° C. have more void volume than the others, as the following results suggest:

<u>Temperature (°C.)</u> <u>of dryers</u>	<u>Sample</u> <u>numbers</u>	<u>Average Vanceometer reading in micro-</u> <u>amperes after 80 seconds penetration time</u>
90	A-E	61
70	F-J	66
50	K-O	67.

Relative penetration of inks with an oil base is commonly controlled by the amount of adhesive per pigment in a coating formulation. The more adhesive present, the less the ink penetrates. This evidence supports that in part D which suggests that the adhesive has penetrated into the raw stock more at the highest drying temperature.

VI. Summary

The seemingly temperature-independent gloss values reported do not agree with those suggested by Yasuda and Stannett (13). Their hypothesis is that an increase in gloss should occur with increasing drying temperature. Of course their amounts of binder in the base stock are higher than that amount used in these coatings.

The I.G.T. print and pick test analysis and the Vanceometer test results both indicate that there is more adhesive penetration into the raw stock at the higher drying temperature. This is an agreement with the suggestion of Yasuda and Stannett (13), who mention that accelerated rates of removal of the vehicle may cause excess penetration of the adhesive.

The decrease in smoothness of the supercalendered, coated sheets with increasing drying temperature can be accounted for by the suggestion of Kraske (9). He believes that a large particle size clay fraction may not have time to align itself in the plane of the raw stock, if the vehicle is removed from the coating too fast.

VII. Appendix

Trial and Error Calculations ... for the components of the ink-picked portion from the I.G.T. print and pick tester, calculated from the ignition products of an ink-extracted sample(all calculations are in grams).

- a. weight of ink-extracted sample .1055
- b. weight of ash .0367
- c. weight lost in ignition .0688
- d. calculated weight of clay assuming all of the ash is clay ignition products typical of a Georgia kaolin*.....(grams of ash \div .8605) = .0426
- e. Amount of casein and Rhoplex B-15 with clay in oven dry coated sheet
(d. times 4% and 8% respectively).....casein .0017
Rhoplex B-15 .0034
- f. (a. minus d. minus e.) equals the weight of paper associated with the coating..... .0578
- g. Calculation of per cent clay in the base stock.

sample	.1104	.0980
ash	.0070	.0065

Assuming that all ignition products are from the clay in the base stock, then the ash \div .8605 = grams of clay on an oven dry basis.

	clay	.0081	.0075
% clay in base stock		7.34	7.65
- h. clay associated with f.....(f. x .075) = .0043
- i. but now d. must be reduced by the amount of clay in h.....(d. minus h.)
= .0383
- j. calculated amount of casein and Rhoplex B-15 from the clay of i.

casein	.0015
Rhoplex B-15	.0031
- k. (a. minus i. minus j.) equals the grams of paper associated with the coating..... .0626
- l. weight of clay associated with the grams of paper of k.
.0047
- m. but now l. reduces d.....(d. minus l.)
.0379
- n. weight of casein and Rhoplex B-15 associated with the clay in m.

casein	.0015
Rhoplex B-15	.0030
- o. (a. minus m. minus n.) equals the weight of paper associated with the coating..... .0631

p. weight of clay associated with the grams of paper of o.....

.0047

q. weight of paper per gram of coating in the picked portion...

$$(o. + p.) \div (m. + n.) = 1.600$$

r. from the data on calculation of the coating weight, there is

$$\frac{1.540 \text{ grams paper}}{5 \times 7 \text{ inches}^2} \times \frac{5 \times 7 \text{ inches}^2}{0.479 \text{ grams coating}} \quad \text{which}$$

equals 3.215 grams paper per gram of coating.

*. Huber, J.M. Corp., Kaolin Clays and Their Industrial Uses, Second Edition,
P.21, New York, N.Y.

Figure II. Vancrometer Reading versus Time Elapsed, for Zero Minutes on Hot Driver

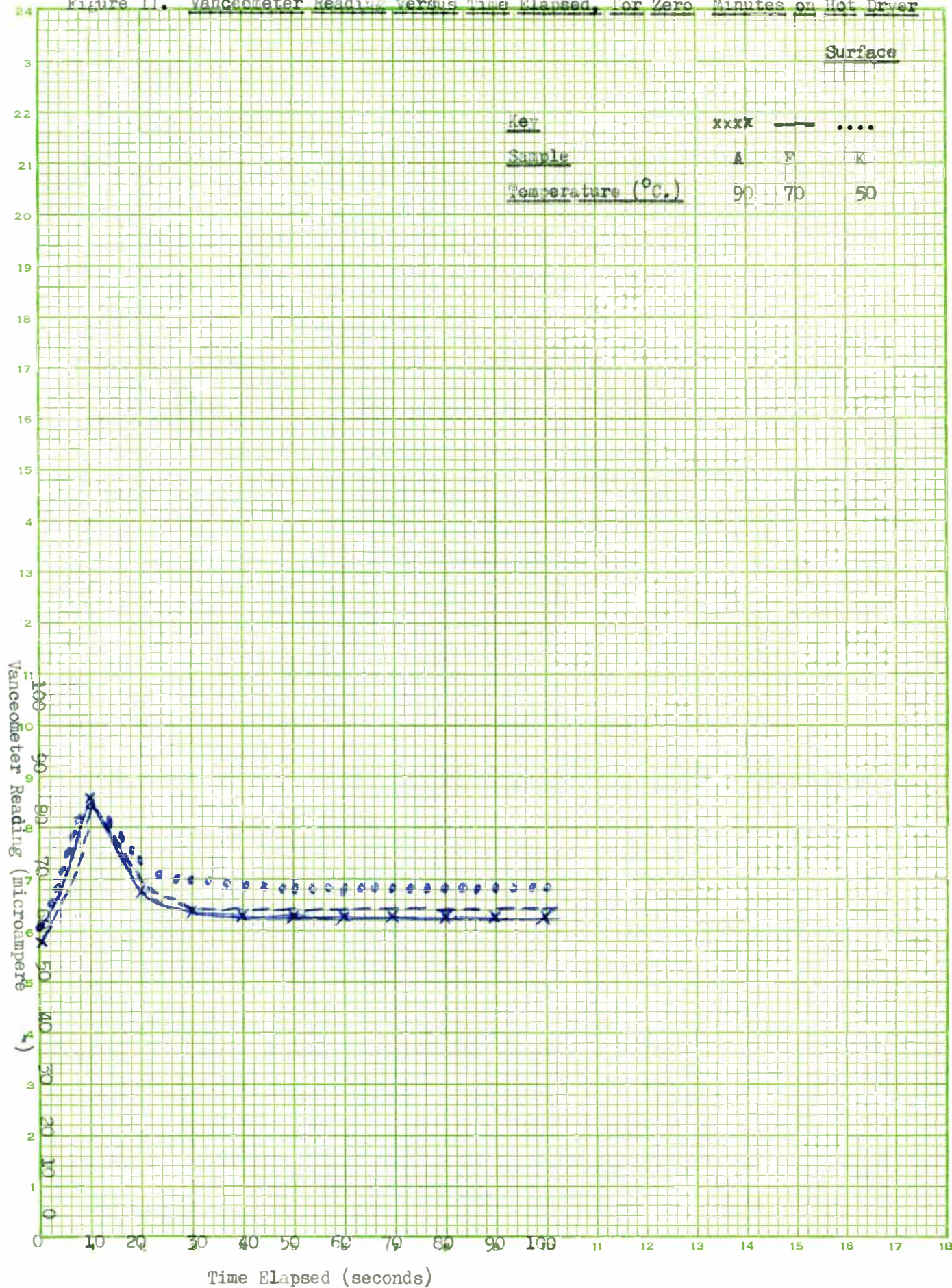


Figure III. Vanceometer Reading versus Time Elapsed, for One-half Minute on Hot/Dryer

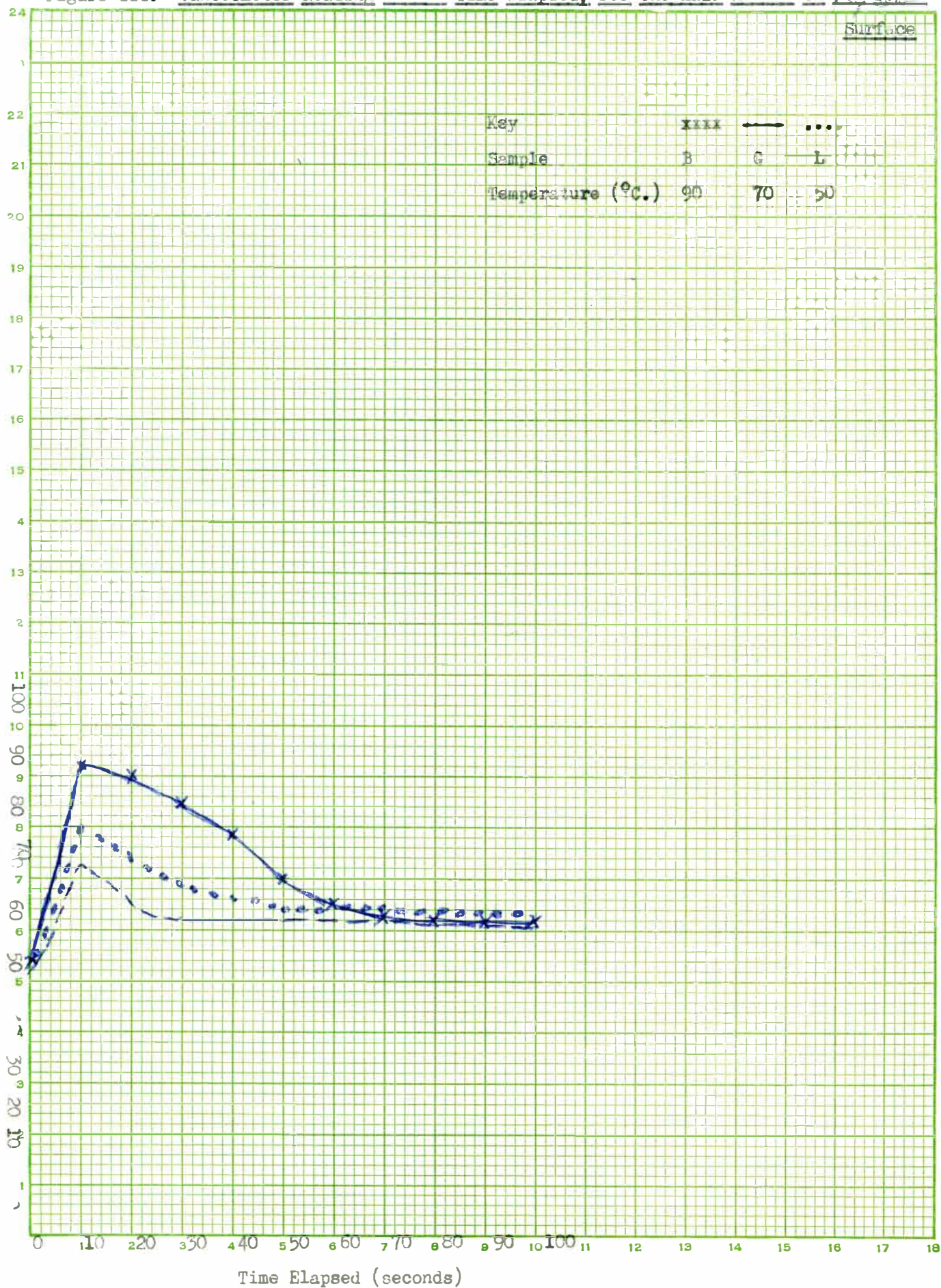


Figure IV. Vanceometer Reading versus Time Elapsed, for One Minute on Hot Dryer Surface

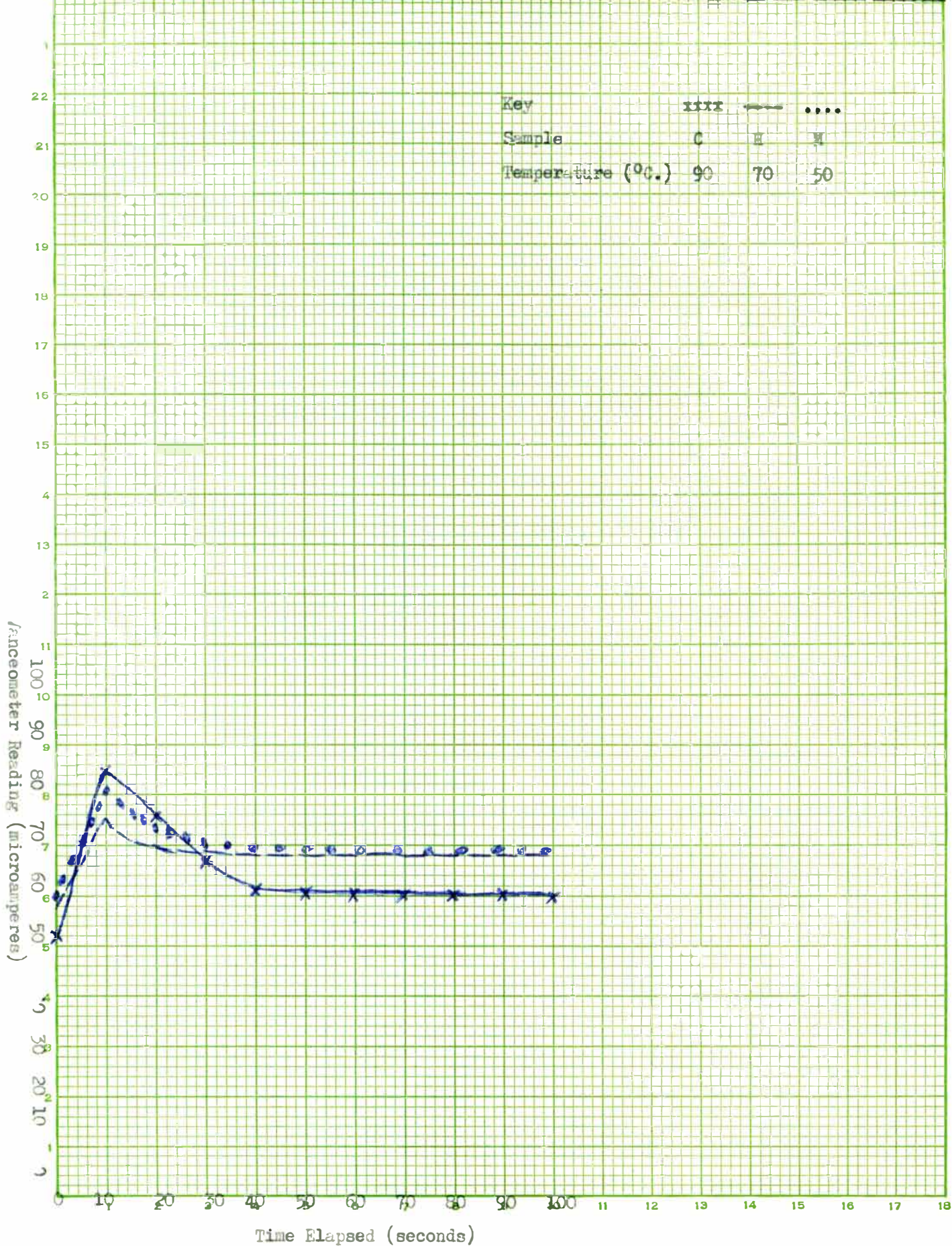


Figure V. Vanceometer Reading versus Time Elapsed, for Two Minutes on Hot Dryer Surface

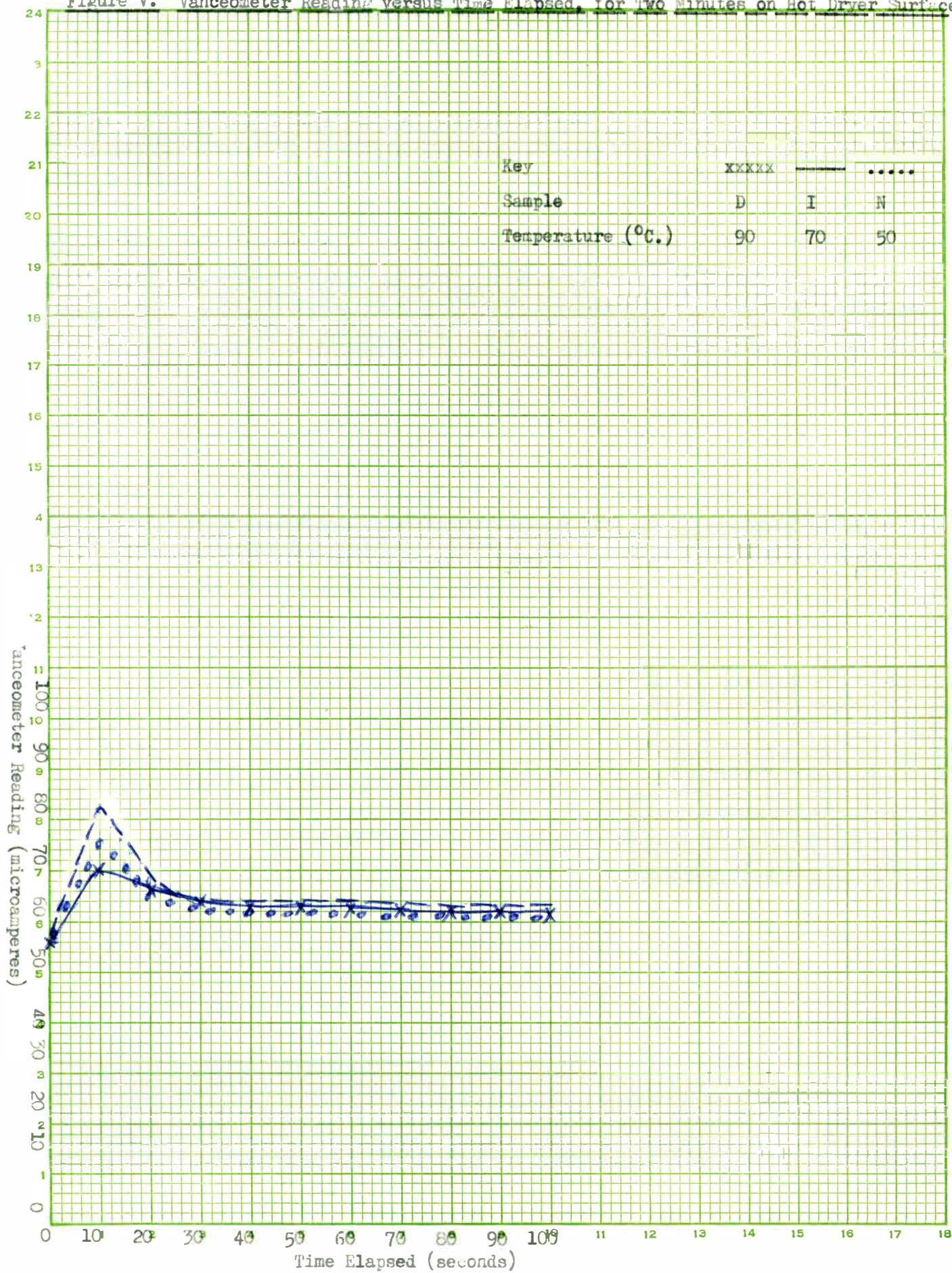
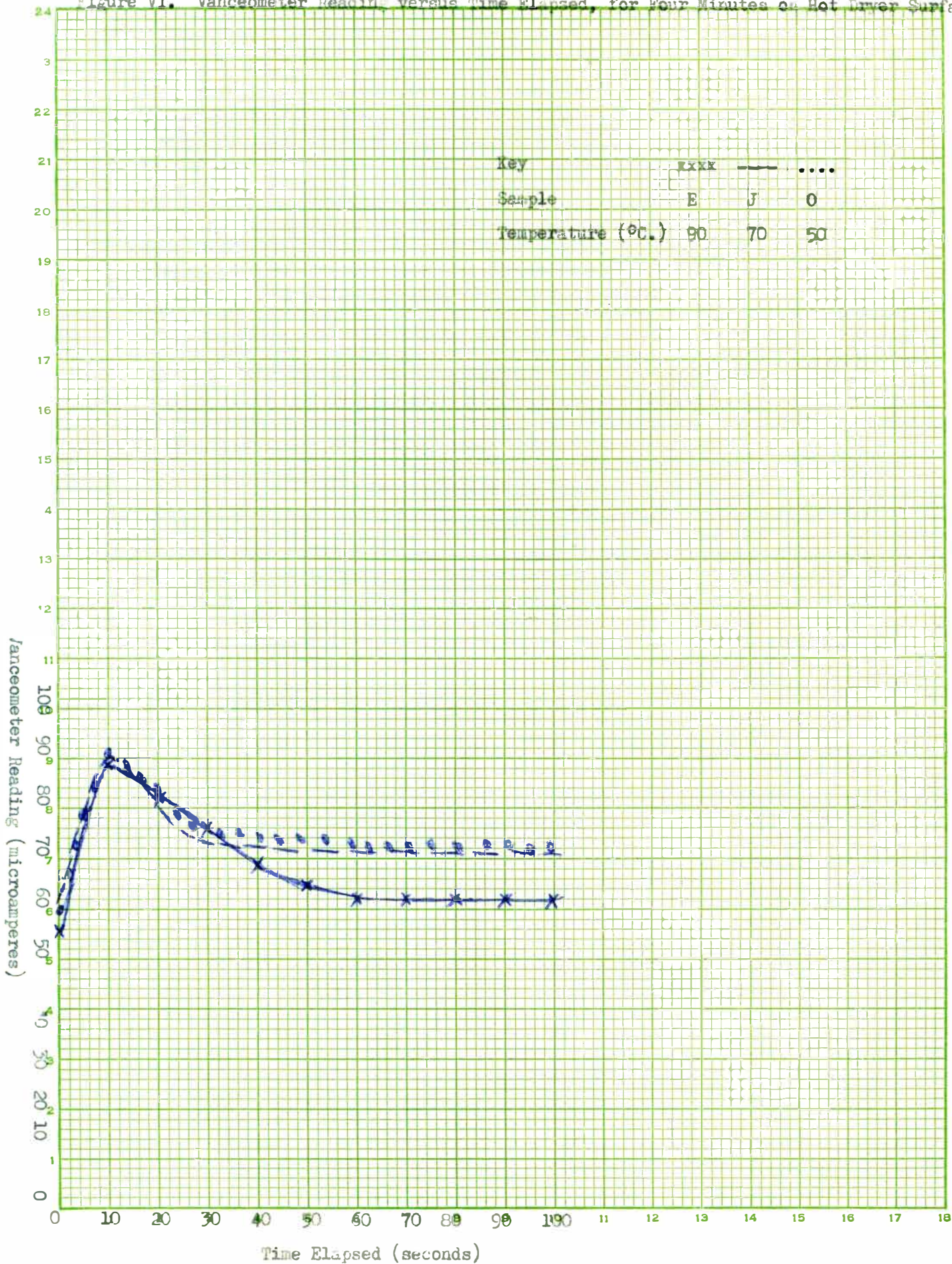


Figure VI. Vanceometer Reading versus Time Elapsed, for Four Minutes on Hot Dryer Surface



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A sincere appreciation to my instructor, Dr.
John Schulz, for his help and guidance throughout
my struggle to complete this research paper.
Thanks again.

Lawrence A. Gaspar