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The Effect of Clay-Adhesive Interaction on
the Structure of Coatings

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THE EFFECT OF CLAY-ADHESIVE INTERACTION ON
THE STRUCTURE OF COATINGS

A thesis submitted by

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SUMMARY

Recently it has been shown that the adhesive plays a significant role in the formation of the film structure for a pigment coating. The adhesive does not merely fill the voids of a predetermined pigment skeleton but, in fact, interacts with the pigment particles and thus changes the film structure. These changes can be characterized by measurement of the pore size distribution and coating film volume. A mercury porosimeter was used to determine both the specific volume of isolated coating films and their pore size and pore size distribution. The coating films were formed on and subsequently isolated from a nonporous tinfoil substrate. The goal of this thesis was to determine the mechanisms by which the adhesive influences the packing of pigment particles in a coating film.

Clay coatings with starch or polyvinyl alcohol (PVA) adhesives were found to form three distinct types of structures as a function of adhesive level. In the range of low levels of adhesive, the volume of the coating film and also the pore size were found to increase with increasing adhesive content. These increases were explained by the adsorption of an adhesive layer on the surfaces of the clay particles which increased the effective particle size. These "encapsulated" particles tend to pack in a less dense manner because of the adhesive layers which separate the clay platelets. An initial maximum in film volume and pore size was found at 2.5 parts PVA or 4.0 parts starch per 100 parts clay. The average thickness of the adsorbed PVA layer was calculated to be 39 Å. and that for starch was 47 Å. The thickness of this adsorbed layer was shown to be independent of the size of the clay particle.

At greater levels of adhesive, there appeared to be no further increase in the thickness of the adsorbed adhesive layers which would affect particle spacing. The coating film volume was found to remain constant over a range of increased adhesive levels. This additional adhesive was therefore free to migrate within the coating structure and to fill the smaller pores during drying.

At higher levels of adhesive, the coating films were found to compact which was indicated by a decreased film volume and a reduction in pore size and pore volume until all pores were filled. Compaction was first observed at 8 parts PVA and 22 parts starch per 100 parts clay. The compaction was believed related to the formation of a "continuum or gel" in the water phase of the coating color as it dried. This gel would encompass the clay particles before the normal pigment skeleton was established and would therefore compact the structure on further drying.

A simplified model was developed which explained the changes in coating structure described above. The majority of the pores in a coating were assumed to be of the slot form and the data from the mercury porosimeter were then used to determine the dimensions of these pores. The width of the slot pores in a coating was shown to be equal to the thickness of the clay platelets. When adhesive was adsorbed on the clay, the spacing between the platelets was shown to be increased by the equivalent of two adhesive layers.

In addition, consideration was given to flocculation and surface tension effects which could have influenced the formation of coating structures. Extensive tests failed to disclose the presence of flocculation in the coating colors which could affect structure. The surface tension changes observed in the coating color also were shown to have no effect on structural formation.

INTRODUCTION

Pigment-coated papers have found widespread acceptance in the paper industry because of their superior appearance and performance characteristics. Pigment coatings are used to mask or improve the appearance of a sheet, to give opacity to a sheet, and to provide an improved printing surface (1). The coating also can provide a special functional surface on a paper such as required for certain duplication processes. In any case, the structure or arrangement of the component parts of a given coating play a significant role in determining the end-use properties of the coating.

There are three basic raw materials used in pigment coatings: (1) the pigment, (2) the adhesive for bonding the pigment, and (3) the vehicle in which the pigment and adhesive are combined. Depending upon the desired effect, the pigments generally used in coatings are clay, calcium carbonate, satin white, and titanium dioxide. Clay is the predominant pigment used in coatings, either alone or in combination with one of the other pigments. In addition to the pigments, the coating film also contains an adhesive material. The main purposes for including an adhesive in the coating are to bind the pigment particles together within the coating film and to bond the film to the paper substrate. The types of binders used vary from natural polymers, such as colloidal starch and casein systems, to many synthetic polymers available as solution or emulsion systems. The vehicle used in most coatings is water.

Past research work in the coating field has emphasized the importance of end-use properties of the coated sheet such as smoothness, gloss, opacity, pick strength, ink receptivity, and printability. Although the evaluation of these properties is important from a quality control standpoint and has been useful in the development and testing of new products, the information obtained from such

tests is necessarily restricted in its interpretation. It has become increasingly evident that more fundamental information is required to gain a better understanding of the complex processes involved in the coating of paper.

There are many variables to be considered in pigment coating. Among the more important are: (1) the types of pigment and adhesives used; (2) the coating mixture variables such as percent solids, rheology, water retention, and pH; (3) the raw stock characteristics, including formation, sizing, strength, and porosity; and (4) the type of coating process and operation variables, such as speed, roll pressures, etc. It is obvious that an extensive study of all of these variables is not feasible in the time available for this study.

Many of the end-use properties commonly used to evaluate coated papers are dependent upon the physical structure of pigment coatings. Coating structure provides a basis for a greater understanding of the variations in the performance of coated papers. Recent work by Burke (2) has shown that the adhesive plays a significant role in determining the structure of pigment coatings. Surprisingly, he found that the adhesive in the coating caused a significant increase in the volume of the pigment film and does not merely fill the voids between the particles in a set matrix. The goal of this thesis has been to attain understanding of the interactions between the adhesive and clay, and the mechanism of the consolidation process which determines the structure of coatings.

BACKGROUND TO THE PROBLEM

Until recently very little work had been done to determine the manner in which a pigment and adhesive combine to form a coating film structure. The term structure, as applied to a coating film, refers to the arrangement of pigment and adhesive components within the film. This may be described or defined in terms of various physical characteristics including density, surface area, pore volume, pore size distribution, and the alignment of the pigment particles relative to one another (2).

The structure of pigment-adhesive films predetermines many of the end-use properties of pigment coatings. For example, variations in the surface areas and pore size distributions of coatings may affect changes in opacity (1). Ink receptivity may be a function of the pore size distribution and total volume of a coating (3). The strength of a coating film is generally considered to be a function of the distribution of the adhesive within the pigment matrix as well as a function of inherent adhesive strength. This distribution of adhesive is thought to be related to the surface area of the pigment (4), pore size distribution within the film (5), and the arrangement of the pigment particles within the film (6).

Several workers have studied the packing characteristics of pigments in an effort to gain an understanding of the coating structure and properties of pigment-adhesive films. Cobb (7) concluded that the amount of a particular coating adhesive required for adequate film strength was governed by the percentage of interpigment voids which were filled with the adhesive material. Willets and Marchetti (8) attempted to explain various coating end-use properties, such as pick strength and gloss, in terms of the volume relationships between pigments and adhesives in coatings. Their experimental results were interpreted to confirm Cobb's relationship between void volume and pigment adhesive demand. Hagemeyer (9, 10) investigated, without the presence of an adhesive, the packing characteristics of pigments which varied in particle size, shape, and chemical composition.

Cobb, Willets, and Marchetti and Hagemeyer made use of the assumption that coating film structures are determined primarily by the packing of the pigment, and that the pigment packs independently of the adhesive present. This phenomenon is commonly referred to as idealized void filling.

Kraske (4) and Eames (5) in their studies on coatings did not claim that a pigment would pack independently of the adhesive. However, they did show that changes in pigment characteristics, such as size of the clay particles in a starch-clay coating film, caused changes in surface area, pore size distribution, and clay platelet alignment within the film. Eames (5) found that for starch-clay coatings formed on a porous substrate, the coatings made from smaller sized clay particles had the greatest strength. When the coatings were formed on a nonporous substrate, there was little change in strength as the clay particles size was varied.

Robinson and Linke (11) employed the concept of idealized void filling for calculating the opacity of pigment-adhesive coatings. Other investigators (12, 13), studying the pick strength and optical properties of pigment coatings containing different adhesives such as starch and polyvinyl alcohol, assumed that the same internal void structure exists no matter what level or type of adhesive was present.

The hypothesis of idealized filling of voids by an adhesive was first tested by Burke (2). The intention of his work was to establish the role of the adhesive in the formation of the structure of pigment coatings. Films from three pigment-adhesive systems (starch-clay, PVA-clay, and latex-clay) were formed on a nonporous substrate and the films from one system (starch-clay) were formed on a porous substrate. The results of his study showed that the hypothesis of idealized void filling was not valid for any of the pigment-adhesive systems investigated and that the adhesive actually increased the interparticle volume reducing the film density. Each of the three adhesives combined uniquely with the same pigment to form widely

differing film structures at equivalent adhesive levels. The structure of the starch-clay film formed on the porous substrate was also markedly different from the same film formed on a nonporous substrate.

The film volumes of Burke's coatings were found to increase and pass through a maximum as the level of adhesive was increased. The amount of increase in film volume and the concentration at which the maximum occurred was shown to be a function of the type of adhesive and substrate used in preparing the coatings. Burke attempted to measure the size of the pores in the coatings by gas adsorption. However, because a majority of the pores had a diameter greater than $0.1\text{ }\mu\text{m.}$, it was only possible to account for 50% of the void volume by this technique. Burke did not accurately characterize the magnitude of the changes which occurred in the structure of the coatings because, unknown to him, the technique for measuring coating film volume increased the thickness of the coating. However, while the magnitude of the data was incorrect, the trends shown by the data for the changes in coating structures were valid.

Burke (2) proposed several mechanisms to explain how each of the adhesives studied could have affected the formation of the film structure. However, these mechanisms were not tested. The present study provides a clearer understanding of the mechanism by which the adhesive influences the structural formation of a pigment coating.

STATEMENT OF THESIS PROBLEM

The objective of this thesis is to determine the mechanism by which the pigment-adhesive interaction influences the structural formation of coating films. Specifically, studies were undertaken to determine what type of pigment-adhesive interaction occurs during the preparation and formation of a pigment coating and what effect this interaction has on the structure of the final coating.

APPROACH TO THE THESIS PROBLEM

To determine the mechanism by which the pigment-adhesive interaction influenced the formation of the structure of coatings, it was necessary first to characterize the type and magnitude of the structural changes occurring in the coating films as a function of adhesive level. Burke (2) was unable to do this adequately because of the limitations of the techniques used in his study. However, with the aid of a mercury porosimeter in the present work, it was possible to measure the overall change in coating film volume as well as the internal changes in pore size and pore size distribution. The initial step in the present study was to make coatings at increasing levels of adhesive and to characterize the structure of each coating. Once this was accomplished, work was directed toward determining the mechanism responsible for the observed changes in coating structure.

Careful consideration of the formation process of the coating structure suggested three plausible mechanisms which could have been responsible for the changes in film structure. The first is a flocculation of the coating particles that could result in an expanded structure. Second, a reduction in the surface tension of the coating colors could have led to a less dense packing of the pigment particles. And third, encapsulation of the pigment particles by the adhesive would lead to an expanded coating structure because of the separation of the clay platelets by layers of adhesive. The first two of these mechanisms had been given strong support in the literature. The third was originally suggested in the present work after study of the formation process.

Burke (2) proposed that the change in structure of pigment coatings at low levels of added adhesive, such as starch or PVA, was due to the polymeric bridging of clay particles. This bridging would prevent the pigment particles from collapsing upon one another as the film is formed. Under this condition the pigment

skeleton of the coating would expand, thus leading to an increase in void volume and specific volume. Further increasing the amount of adhesive after the point of maximum film expansion was reached caused the pigment skeleton to collapse or compact. The result was a decrease in void volume and specific volume. Burke proposed that in this region the adhesive was acting as a lubricant permitting the clay particles to slip past one another and pack in a more dense manner. The overall phenomenon was believed related to a flocculation mechanism.

La Mer, et al. (14, 15) have shown that polymer materials, including starch, can bridge or flocculate pigment particles and cause an expanded and more porous pigment-polymer structure. La Mer measured the extent of flocculation using filtration rates which were determined by passing the filtrate back through the formed filter cake of coating material. These filtration rates increased as the amount of polymer was increased up to an optimum concentration of flocculant. At this point there was a maximum in floc size and porosity of the filter cake. Upon further addition of flocculent there was a decrease in floc size and, hence, in the filtration rate. This was believed due to the protective and peptizing action of the flocculating agent. Consequently, a series of experiments was conducted in the present work to determine if flocculation was occurring in the coating colors and if the flocculation was the result of a pigment-polymer bridging or the result of some other type of interaction.

McEwen (17), in a study of the role of water in the starch-clay-water paper coating system had hinted that starch could possibly "rob" the dispersing agent from the clay causing the clay to flocculate. To test for this type of flocculation, low shear viscosity measurements could be made of a clay-water slurry which had been in contact with a starch solution but separated by a viscose membrane. An increase in low shear viscosity would indicate the presence of flocs which may or may not be highly stable.

The second possible mechanism investigated in this study concerned the effect of reduced surface tension of the coating colors on the packing characteristics of pigment particles as the level of adhesive was increased. Duff (18) had shown that surface tension determined the capillary pressure which develops as the water recedes during the drying of a pigment film. Water has a high surface tension and exerts a positive capillary pressure on clay. This would pull the clay platelets together and form a compact pigment film. If the surface tension is changed, either by the effect of the binder present or by added surfactants, the lower capillary pressures could result in less dense pigment packing and an expanded film volume. However, the question is one of how great the effect of surface tension can be on the packing of rigid pigment particles.

The third mechanism involved adsorption of the adhesive on the surface of the pigment particle which would tend to increase the effective particle size of the pigment. These larger encapsulated or coated particles would be expected to pack in a less dense manner due to the layers of adhesive separating the clay platelets. In testing this mechanism, it was necessary to determine if the change in particle thickness due to the adsorbed adhesive was great enough to account for the observed increase in coating film volume. It was expected that if particle encapsulation was occurring, the thickness of the adsorbed layer of adhesive would be the same on different sized clay platelets. Therefore, it was expected that coatings made from larger clay particles would exhibit less of an increase in film volume because the relative increase in particle size would be less.

The objective of this work was to determine what type of interaction occurs between the pigment and adhesive and how it influences the structural formation of pigment coatings. The experimental approach involved first determining what changes occurred in the structure of the coatings. This was followed by evaluation of the

possible mechanisms for the changes in the structure. These mechanisms included flocculation of the coating particles, reduction in the surface tension of coating colors, and pigment encapsulation by a layer of adhesive.

EXPERIMENTAL PROCEDURES

The choice of the materials and experimental procedures used in this study was influenced by the objective of this thesis which was to determine the reason for the expanded coating structures observed by Burke (2). The coating systems and conditions were selected to correspond closely to those employed in the previous study. The following discussion of experimental procedures describes the techniques used in the present work and points out changes which were found necessary from those used in Burke's investigation.

DESCRIPTION OF COATING MATERIALS

CLAY

The pigment selected for this work was kaolin clay. Three different clay samples were chosen because of the variation in their particle size. The majority of the work in this thesis was carried out using Type 2X clay (an experimental clay developed by the Georgia Kaolin Company) which was chosen because it had a narrow particle size range similar to that of Burke. Thus, laboratory fractionation of the clay was not necessary. A sample of a delaminated clay was chosen because of its large particle size. This sample (Nu-Clay, manufactured by Freeport Kaolin Company) was further fractionated to remove any remaining small sized clay particles. The third clay sample was that which remained from Burke's investigation.

The size of the clay particles for all three clays was determined from electron micrographs from measurements made on a microcomparator. The size of the particles was characterized in two dimensions, length and thickness. Clay particles are normally hexagon-shaped platelets in which the length and width are approximately equal. The thickness of the clay platelet particles was determined by measuring the length of the shadows cast by the particles in the electron micrographs. The

distributions of particles lengths and thicknesses are given in Appendix I. The number average particle dimensions are given in Table I.

TABLE I
CLAY PARTICLE SIZE DIMENSIONS

	No. Av. Length, μm .	No. Av. Thickness, μm .	Length/ Thickness
Type 2X clay	0.438	0.049	9.0
Burke's clay	0.921	0.088	10.5
Fractionated Nu-Clay	5.06	0.506	10.0

The length-to-thickness ratio for the three clays is approximately the same, indicating that the particles have generally the same shape and differ only in size.

The clays were dispersed in distilled water containing the appropriate amounts of dispersing agent and NaOH at approximately 70% solids. The amount of dispersing agent (Quadrafos) used was that required to give a minimum Brookfield viscosity to the clay slurries in the manner described by Kraske (4). The pH of the clay slurries was adjusted to 9.0 with 1.0N NaOH. Type 2X clay and Nu-Clay were found to be pre-dispersed by the manufacturer and required less dispersing agent than Burke's clay. The amount of dispersing agent and NaOH required for the three clays is given in Table II and expressed in milliequivalents per 100 g. of clay.

TABLE II
DISPERSING AGENT AND NaOH REQUIREMENTS OF CLAY SLURRIES

	Amount Dispersing Agent, meq./100 g. clay	Amount of NaOH, meq./100 g. clay
Type 2X clay	0.3	2.9
Burke's clay	3.0	3.0
Nu-Clay	0.0	3.0

ADHESIVE

The adhesives selected for this study were starch and polyvinyl alcohol (PVA). The starch used was a dextrinized starch (Clinton 632) manufactured by the Clinton Corn Processing Company. The polyvinyl alcohol selected was Du Pont's Elvanol 71-30. This is a fully hydrolyzed, medium-range molecular weight material that is generally recommended as a pigment coating binder.

The starch was cooked at 35% solids in a stainless steel beaker immersed in a water bath. Mixing was provided by a propeller-type blade attached to a Lightnin' mixer. This type of mixing was found to give a better dispersion of starch than when cooked using Corn Industries Viscometer (C.I.V.). The starch first was dispersed in cold distilled water, the temperature then raised to 96°C. and held at this point for 30 minutes. After the cooking period the slurry was cooled to 50°C. and kept at this temperature until used (not longer than 3 or 4 hours). The polyvinyl alcohol was prepared in the same manner at 5% solids.

SUBSTRATE

The substrate used in all coatings was 0.0015-in. gage tinfoil obtained from E. H. Sargent Company in rolls 12 inches wide. This foil represents a nonporous substrate from which the coating film could be readily isolated. The foil eliminated the variable of substrate porosity, which may exert an influence on the role of an adhesive in structural formation, such as migration of the adhesive into a porous substrate.

PREPARATION OF COATING COLORS

All the coating colors were prepared in the following general manner. The clay slurries were dispersed at approximately 70% solids using the required amounts of Quadrafos and NaOH. Mixing was provided by a Lightnin' mixer using a propeller-type

blade. In preparing the actual coating formulation, it was found desirable to add the clay slurry (at 70% solids) to the adhesive as it was being mixed with a Hamilton Beach stirrer. This provided the best conditions for the adhesive to be evenly distributed throughout the clay pigment. Water was then added to give the specified solids content, 50% for starch-clay and 30% for PVA-clay coating colors. The colors were made up in 50-g. total weight batches. The pH of the colors was adjusted to 9.0 with 1.0N NaOH and mixing continued for 30 minutes after which the coatings were screened through a 325-mesh screen. Each color was deaerated for 15 minutes at a pressure of 2 p.s.i.a. while being agitated with a magnetic stirrer.

COATING APPLICATION AND DRYING CONDITIONS

The coating colors were spread on the tinfoil with a Boston-Bradley Adjustable Blade applicator bar (19). This applicator bar is similar to a Bird Bar except that it is possible to vary the clearance between the bar and the substrate. The quantity of pigment applied per area of substrate was kept essentially constant for most films by varying the wet film thickness applied and the color solids. The tinfoil was laid on a moistened glass surface, pressed flat, and taped in place on all four sides with cellophane tape. This procedure assured that the substrate would be flat during application and drying of a film. A puddle of coating color was then placed on the foil and spread with the applicator bar.

All films were dried under the mild conditions of 73°F. and 50% R.H.

ISOLATION OF COATING SAMPLES

Coating films formed on tinfoil substrates were isolated by dissolving away the foil in mercury. Samples were placed, foil side down, on pools of mercury held in culture dishes. After 30 minutes, the sample could be removed from the surface of the mercury using a spatula. The substrate side of the sample was then brushed with

a small brush to remove any remaining mercury-tin amalgam. Any amalgam still remaining can be removed from the sample by rubbing with soft facial tissue while the sample is lying on a flat glass surface. One contact with a fresh mercury surface was generally found to remove all of the tinfoil.

PHYSICAL MEASUREMENTS OF COATING FILMS

FILM DENSITIES

The density measurement of interest in the pigment coating field is the apparent density, or the weight of material per total film volume (volume of pigment + volume of adhesive + volume of voids). There are many techniques described in the literature for determining the apparent density and these are reviewed by Burke (2).

The method used by Burke for measuring film densities was based upon a direct measurement of the weight and volume of the samples. The technique is briefly discussed in the following section and note is made of several modifications which were found necessary.

Burke's density technique involved taking a sample of the coating film approximately 2.5-cm. square and removing a strip 0.5-cm. wide from adjacent sides of the square. These two strips were used for thickness measurements while the remaining 2.0-cm. square was used to determine the weight-per-unit-area. The area was determined from a polaroid picture of the square sample at 3.16X by a planimeter measurement of the image on the picture. The sample weight was determined on a semimicrobalance after the sample had been dried at 100°C.

An accurate measurement of film thickness is most critical in determining the apparent density by this technique. Burke mounted the thickness samples in butyl methacrylate then microtomed or cross sectioned the samples along the side which

adjoined the periphery of the weight/area sample. The cross sections were photographed at 300X and planimetered to obtain an average thickness.

In the course of the present study, it was determined that mounting the starch-clay coatings in butyl methacrylate caused a 15% increase in thickness of sample. Burke tried to detect any change in thickness due to embedding in butyl methacrylate by comparing the thickness values of a duplicate sample which had been embedded in an epoxy material, Epon 812. It appears that both materials swell the coatings to the same degree.

Two other techniques were used in the present study to measure film thickness. One involved using the IPC Fiber Load-Elongation Recorder (20) which had been converted to a microcaliper gage. Changes in thickness of $\pm 0.54 \mu\text{m}$. can be measured directly with this instrument. The second method employed for determining the film thickness involved placing the sample on edge and measuring the thickness through a microscope at 450X using a calibrated eyepiece micrometer. The thickness could be read directly to $\pm 1.16 \mu\text{m}$. using this technique. The values for film thickness determined by these two techniques agreed closely. However, it was found that a more accurate measurement of film density could be obtained using the mercury porosimeter.

The film density measurements in the present work were determined using the Aminco Digital Readout Porosimeter, 15,000 p.s.i. Model made by the American Instrument Company. The coating sample is placed in the penetrometer (a glass tube with a graduated capillary stem), the filling device is evacuated to a pressure of 50 μm . and then the penetrometer is permitted to fill with mercury. The density measurement is made at 11.3 p.s.i.a. which is the pressure on the sample at atmospheric conditions corrected for the mercury head in the penetrometer stem.

The density values obtained by the mercury porosimeter agree closely with those obtained by measuring the weight and physical dimension of the coating samples. A comparison of the values obtained by the two different techniques is given in Appendix II. The greater precision, $\pm 1\%$, of the density measurements obtained using the mercury porosimeter dictated its use in the present study.

PORE SIZE DISTRIBUTION

The mercury porosimeter has proven to give a reliable measurement of the pore size of porous materials (21). When a rigid porous material is immersed in a non-wetting liquid and subjected to continuously increasing pressure, a curve characteristic of that material is obtained by measuring the total cumulative volume of liquid forced into the pore system at each pressure.

The theoretical basis for the mercury penetration technique is negative capillarity. In any system consisting of a porous solid and nonwetting liquid there is an opposition to the entry of the liquid due to the surface tension forces. Pressure is therefore required to cause the liquid to enter any pore and the pressure required increases as the pores become smaller. The relationship which gives the pressure required to force liquid into a cylindrical pore of given size is:

$$P_c = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \cos \theta \quad (1)$$

where

$\underline{P_c}$ = capillary pressure,

$\underline{R_1}$ and $\underline{R_2}$ = radii of pore in major and minor directions,

γ = surface tension of liquid,

θ = contact angle of liquid on solid.

When the applied pressure, P , is equal to or greater than the capillary pressure, the capillary will fill with mercury. The derivation of this equation is reviewed by Ritter and Drake (22). For the case where the pore is a slit between two parallel plates and thus $R_1 \ll R_2$, then $1/R_2$ is small compared to $1/R_1$ and Equation (1) becomes:

$$P = - \frac{\gamma \cos \theta}{R_1} \quad (2)$$

The difference between Equations (1) and (2) can be as much as a factor of 2.0 depending on the shape of the pore. Generally, Equation (1), which describes a model consisting of ideal cylindrical capillaries, is used to interpret porosimeter results. However, it is possible that Equation (2) might better describe the pores which exist in a coating because it is made from flat clay platelets.

Drake (23) has indicated that the surface tension of mercury remains constant over the range of pore size measured in this study. The remaining variable in Equations (1) and (2) is the contact angle of mercury. Values from 110° to 145° have been reported in the literature (22). An attempt to measure the contact angle of mercury on clay coatings is described in the next section.

The coating samples were prepared for pore size measurements by first removing the tinfoil substrate. The samples were then cut into 0.8 x 2.5-cm. strips and oven dried at 100°C . for one hour. The samples were kept in a vacuum desiccator until measured. The powder type of penetrometer was used in the porosimeter because of the tendency for weak coatings to break into small pieces. Each coating sample was evacuated to 50 μm . pressure before weighing in an effort to remove any remaining moisture.

The data from the porosimeter can be presented in two forms. The first is a plot which shows the cumulative volume of mercury which has penetrated into the porous material versus the pressure required to cause the penetration. A more

instructive form is obtained by differentiating the cumulative volume plot which results in a volume frequency vs. pressure distribution curve. This is the form in which the data are presented in the present study.

CONTACT ANGLE MEASUREMENTS

The value of pore size calculated from Equation (1) changes significantly depending upon the contact angle chosen. Therefore, an attempt was made to measure the contact angle of mercury on the coating films which had been conditioned to the environment that exists in the porosimeter.

Six coating samples were chosen for the contact angle measurements. Burke's clay and Type 2X clay films were prepared with no adhesive. The other coatings were prepared using those same clays with starch and PVA as adhesives. The samples were placed in a vacuum desiccator and evacuated to a pressure of 50 μ m. The desiccator containing the samples under vacuum was then placed inside a plastic bag which completely enclosed a Rome-Hart Inc. Goniometer. The air was purged from the plastic bag with N_2 gas that had been passed through liquid nitrogen and a desiccator train to remove any moisture. Dishes of P_2O_5 had been previously placed in the bag to aid in removing any moisture present. The desiccator was unsealed and the coating samples removed, using plastic gloves which were part of the plastic bag. Fresh mercury drops were placed on the surface with a hypodermic syringe. Thirty-five mm. pictures were taken of the mercury drops sitting on the coating surfaces.

The contact angles were measured from the photographs using a specially adapted tangentometer. The contact angle for all coating samples was approximately the same, $155^\circ \pm 2^\circ$. This value is higher than those previously reported in the literature (22). The high value is possibly attributed to the fact that the coating samples are not completely dried under the conditions which exist in the porosimeter. Glossman (24) indicated that the last remaining layers of water are firmly held and are possibly

oriented with the hydrogen atoms extending away from the surface of the solid. This results in a lower critical surface tension, γ_c , (25, 26) and increases the contact angle. If these last remaining layers of water were removed, the contact angle would be expected to decrease. However, the coating samples are not completely dried in the porosimeter. The value of 155° for the contact angle is considered to be the most accurate in that it was measured under the condition which exists in the porosimeter when the pores are actually being measured.

EXPERIMENTAL TECHNIQUES USED IN FLOCCULATION STUDIES

The flocculation hypothesis was investigated with a series of experiments. Filtration rate studies were made of dilute coating colors to determine if flocculation was occurring by polymeric bridging. Low shear viscosity measurements were made of clay slurries in an adhesive diffusion study to determine if the binder had the ability to "rob" the dispersing agent from the clay and cause flocculation. Viscosity measurements to detect flocculation were made of coating colors at various levels of adhesive. Finally, measurements were made of possible changes in the size of the coating particles before and after the addition of an adhesive.

A detailed description of the techniques and equipment used in the flocculation studies is given in Appendix III.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

It will be helpful to keep in mind throughout the following discussion that the experimental approach in this thesis was to first characterize the type and magnitude of the structural changes occurring in the coating film as a function of the adhesive level. This was followed by the evaluation of the possible mechanisms of which one or all could have been responsible for the changes occurring in the coating structure. These mechanisms included flocculation of the coating particles, reduction in the surface tension of the coating colors, and pigment encapsulation by a layer of adhesive.

STRUCTURE OF COATINGS

In studying the interaction between a clay pigment and an adhesive in coatings, it is helpful to visualize how the structure of the coating film is established. This is shown in a graphical manner in Fig. 1. This figure shows the volume relationships of the pigment, adhesive, and vehicle from the time the coating color is applied until the final film structure is established.

The diagram is based on a constant volume of 1 gram of clay and increasing amounts of adhesive. The line at the top of Fig. 1 indicates the volume of the coating color at the time of application. The horizontal dashed line represents the volume of the final coating film if the adhesive simply fills the voids in the pigment matrix. The position of this line is determined from the volume of a clay film containing no adhesive. The volume of voids is the difference between the volume of the final coating film and the sum of the volumes of clay and adhesive. A continuous film exists when all of the voids have been filled and the line representing the volume of the coating film extends upward with a slope of 1.0. This slope is the result of added increments of binder causing equal increments of increase in the volume of film containing 1 gram of pigment. The point at which

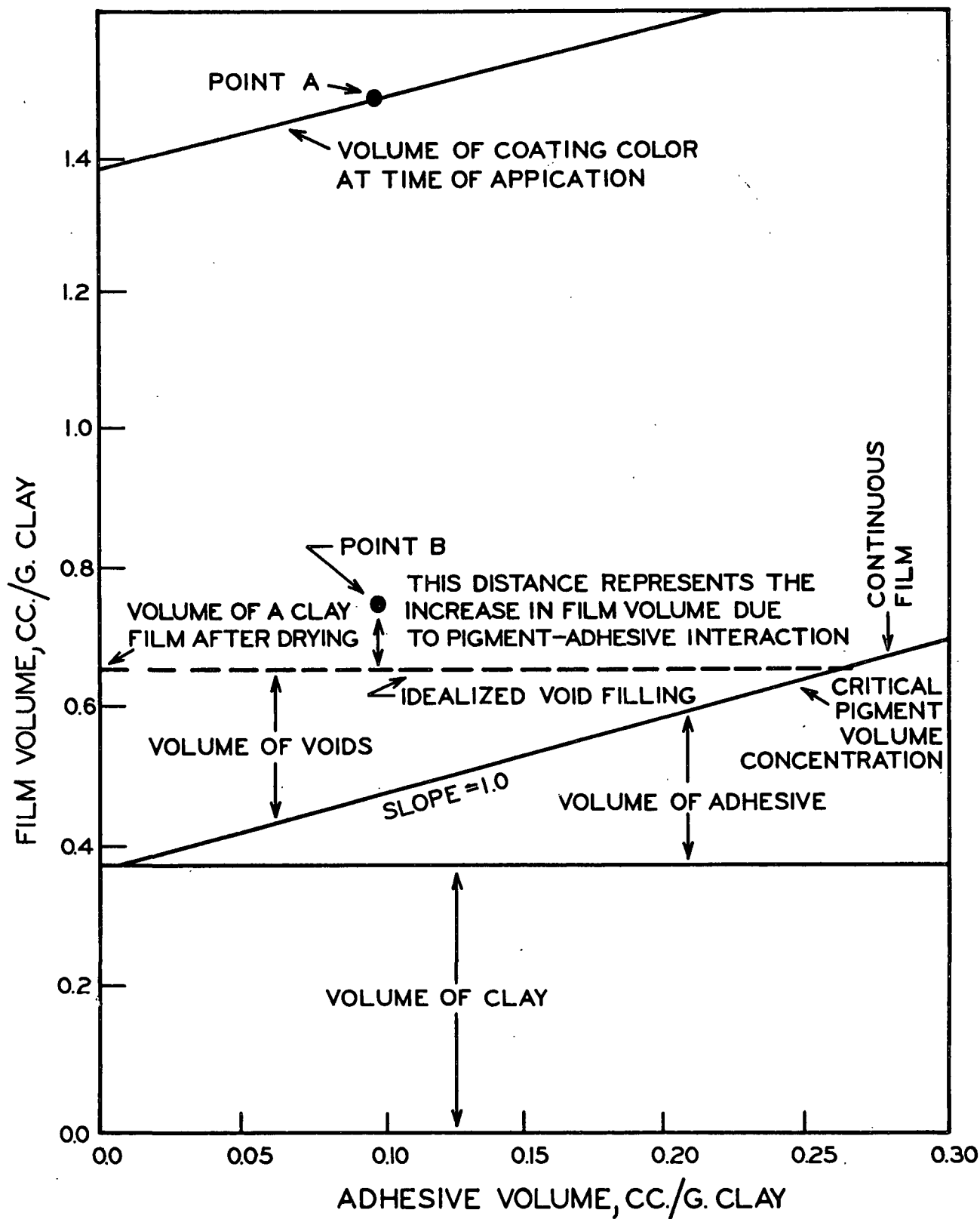


Figure 1. Changes in Film Volume per Gram of Clay with Changes in Adhesive Volume per Gram of Clay for Clay Coatings

the idealized void filling line intercepts the line representing the sum of the adhesive volume plus the clay volume is called the critical pigment volume concentration (C.P.V.C.). The C.P.V.C. (8) is defined as the level of pigmentation in a dried coating film at which there is just enough adhesive present to fill the voids between the pigment particles.

The volume of the coating color when applied to the substrate is represented by Point A. Immediately after the application of the wet coating film to the nonporous substrate vehicle evaporation begins. This evaporation takes place at the air-film interface and the thickness of the wet film decreases in a direction normal to the substrate (the z-direction). As the thickness decreases, the pigment particles in the wet film are brought closer and closer together. At the same time the concentration of the adhesive present in the liquid phase is increasing. The volume of the coating color is being reduced from Point A to Point B in Fig. 1.

Finally, enough evaporation has taken place so that the pigment particles begin to contact one another, or are separated by associated adhesive material and perhaps small amounts of concentrated adhesive material. When this stage is reached, the pigment particles are probably immobilized, or certainly greatly hindered from further movement. From this point on, a definite skeleton or pore structure begins to establish. Evaporation continues at the film surface as long as the pore or capillary system established is capable of supplying liquid. The vehicle or evaporation interface gradually recedes into the coating as the supply rate diminishes. Then menisci begin to form in the capillary skeleton of the coating. When these menisci form, surface tension forces similar to those discussed by Duff (18) and Haines (27) are exerted on the structure. As the vehicle menisci retreat further, the contracting forces of the menisci are replaced partially by the final adhesive bonds which hold the pigment particles together. The volume of the coating by this time has reached Point B in Fig. 1 and is a rigid, porous, pigment adhesive structure.

The value of Point B lies above the line representing idealized void filling because, as shown later, the coating structure ends up in an expanded state due to an adhesive-pigment interaction.

TYPE 2X CLAY-DEXTRIN STARCH COATINGS

The initial step in this study was to characterize the overall as well as the internal changes which occur in the structure of coatings films as the amount of adhesive was increased. The changes in film volume per gram of clay vs. changes in dextrinized starch volume per gram of Type 2X clay is shown in Fig. 2. The tabulated data from which Fig. 2 were prepared are given in Appendix I, Table VIII.

The data points for the film volumes of starch-clay coatings do not fall on the dashed line representing idealized void filling. These experimental values show that the coating film volume increased with added increments of the starch until a maximum was reached. The maximum was reached at a weight fraction pigment, $\frac{f_p}{p} = 0.96$ (4 parts starch/100 parts clay) and was determined to be about 0.74 cc./g. clay as compared to a film volume of 0.65 cc./g. clay for the clay pigment film alone without starch binder present.

Once the maximum was reached there was a range of pigment fractions over which increasing increments of starch did not change the film volume. This region extends to about $\frac{f_p}{p} = 0.82$ (22 parts starch/100 parts clay). Further increases in the amount of starch resulted in a decrease in film volume. The curve drawn through the experimental values intercepts the line representing the sum of the volumes of starch and clay at the critical pigment volume concentration.

The structure of the starch-clay films underwent three distinct changes as the amount of adhesive was increased. First, there was an initial expansion of the film followed by a region in which the film volume remained constant. Finally, the volume

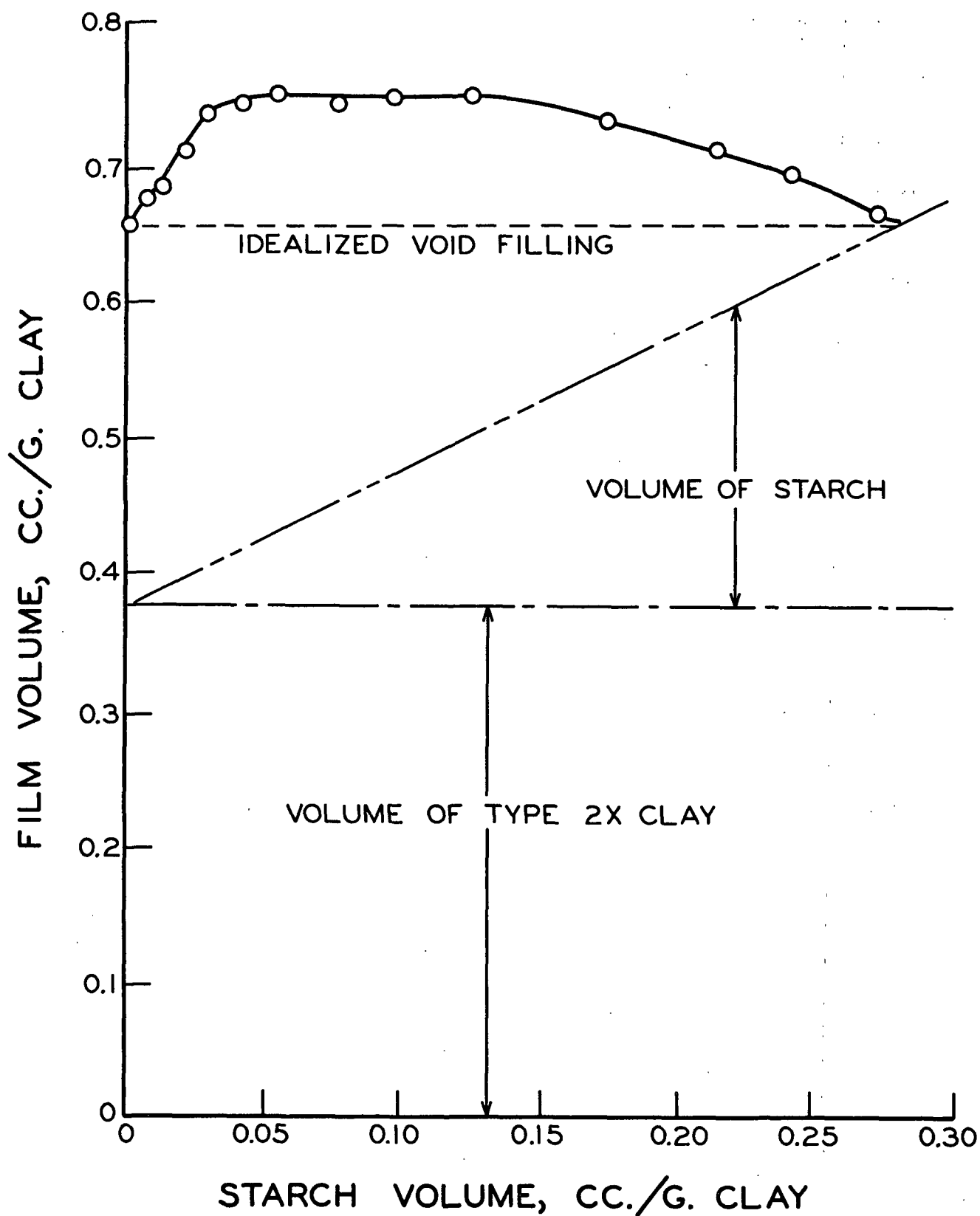


Figure 2. Changes in Film Volume per Gram of Clay with Changes in Starch Volume per Gram of Clay for Type 2X Clay-Starch Films

decreased, indicating the formation of a more compact structure. These changes in overall film volume can be better understood after considering the changes which take place in the internal coating structure.

The change in pore size and pore size distribution for the region in which the starch-clay films were expanding in volume is shown in Fig. 3. The position of the peaks from the frequency distribution curve are listed in Appendix IV, Table XIII. As the amount of starch was increased, the pressure required for intruding the pores with mercury decreased from 1860 to 1210 p.s.i. which indicated that the pores were becoming larger. The pore size dimensions given in Fig. 3 are based on Equation (2) with a contact angle of 155° .

The pore volume frequency vs. pore size distribution curves for the region where the volume of the starch-clay coatings remained constant as the amount of starch was increased are shown in Fig. 4. It should be noted that the size of the large pores remained constant while the small pores appeared to be filling with starch. This filling of the small pores is indicated by the leftward movement of the high pressure side of the distribution peak. This movement is pointed out with an arrow in Fig. 4.

The picture of the internal pore size distribution is completed with Fig. 5 which covers those starch levels where the volumes of the coating films were decreasing. In this range the larger pores decreased in size and the frequency peak became narrower until all pores were filled.

These foregoing results have shown that the film volume and average pore size of Type 2X clay-dextrinized starch films increased when initial increments of starch were added. After the initial increase in film volume, the structure essentially remained at a constant volume with the added starch going to fill the smaller pores.

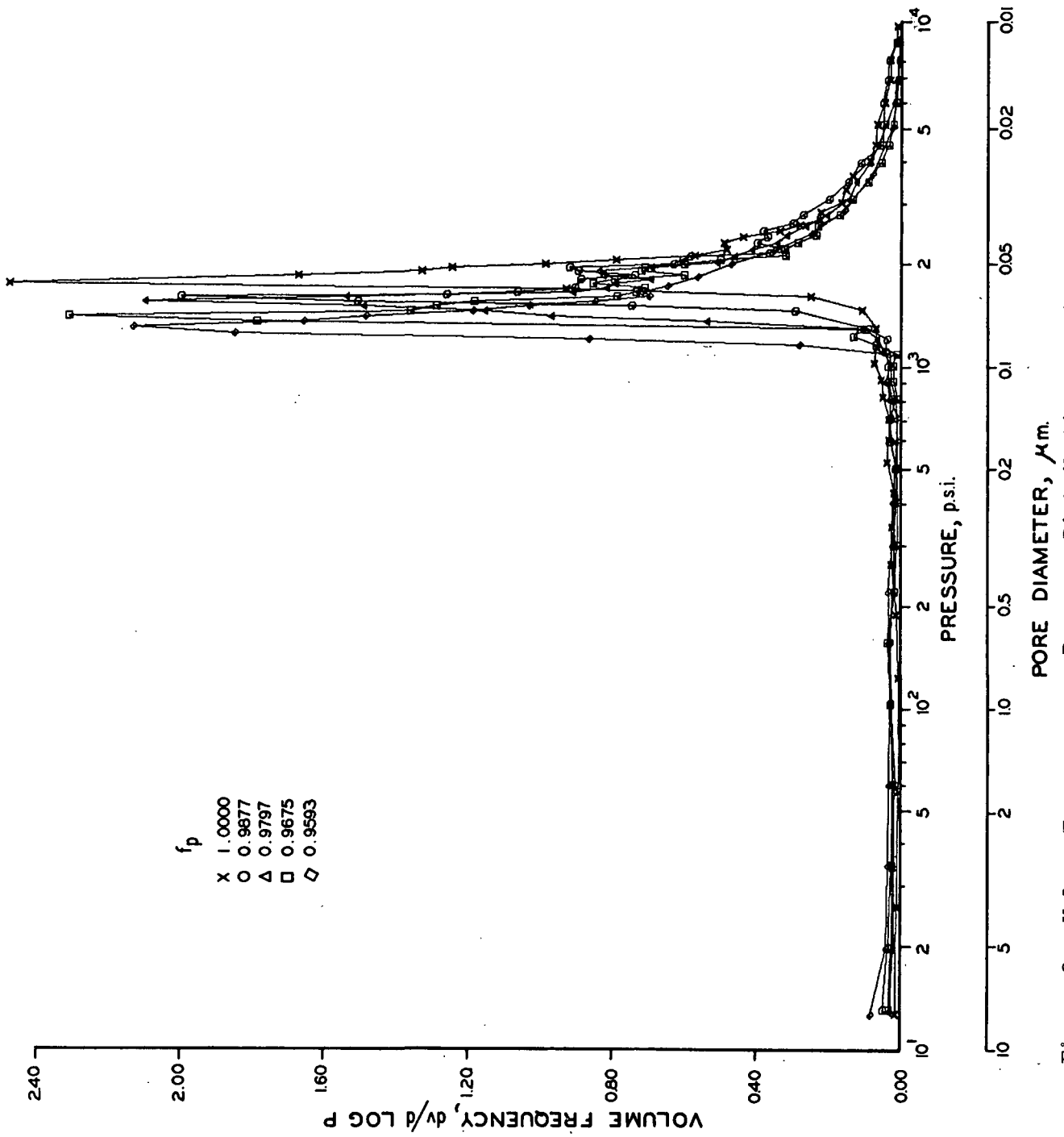


Figure 3. Volume Frequency vs. Pressure Distribution for the Expanding Structures of Type 2X Clay-Starch Coatings

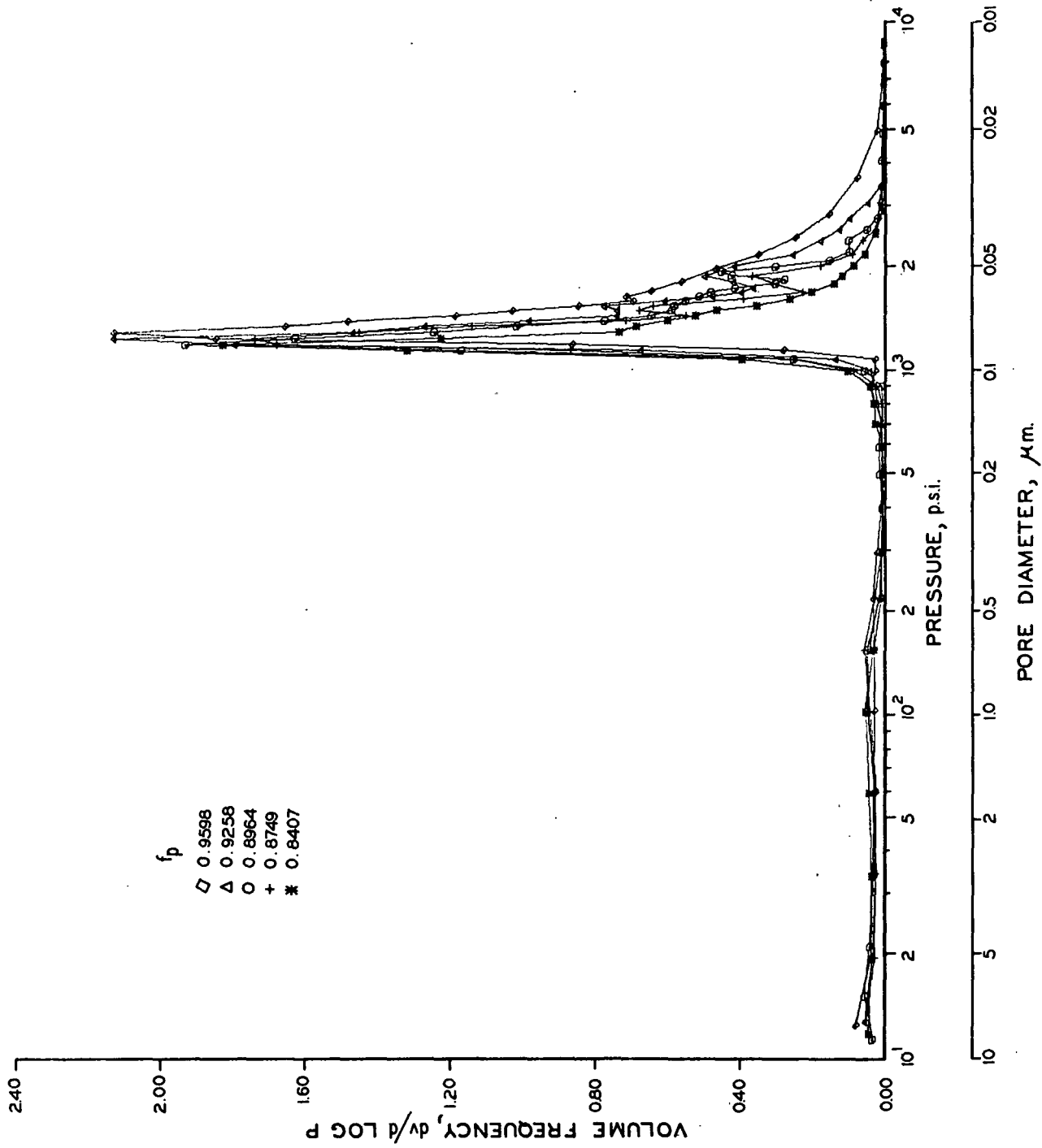


Figure 4. Volume Frequency vs. Pressure Distribution for the Constant Structures of Type 2X Clay-Starch Coatings

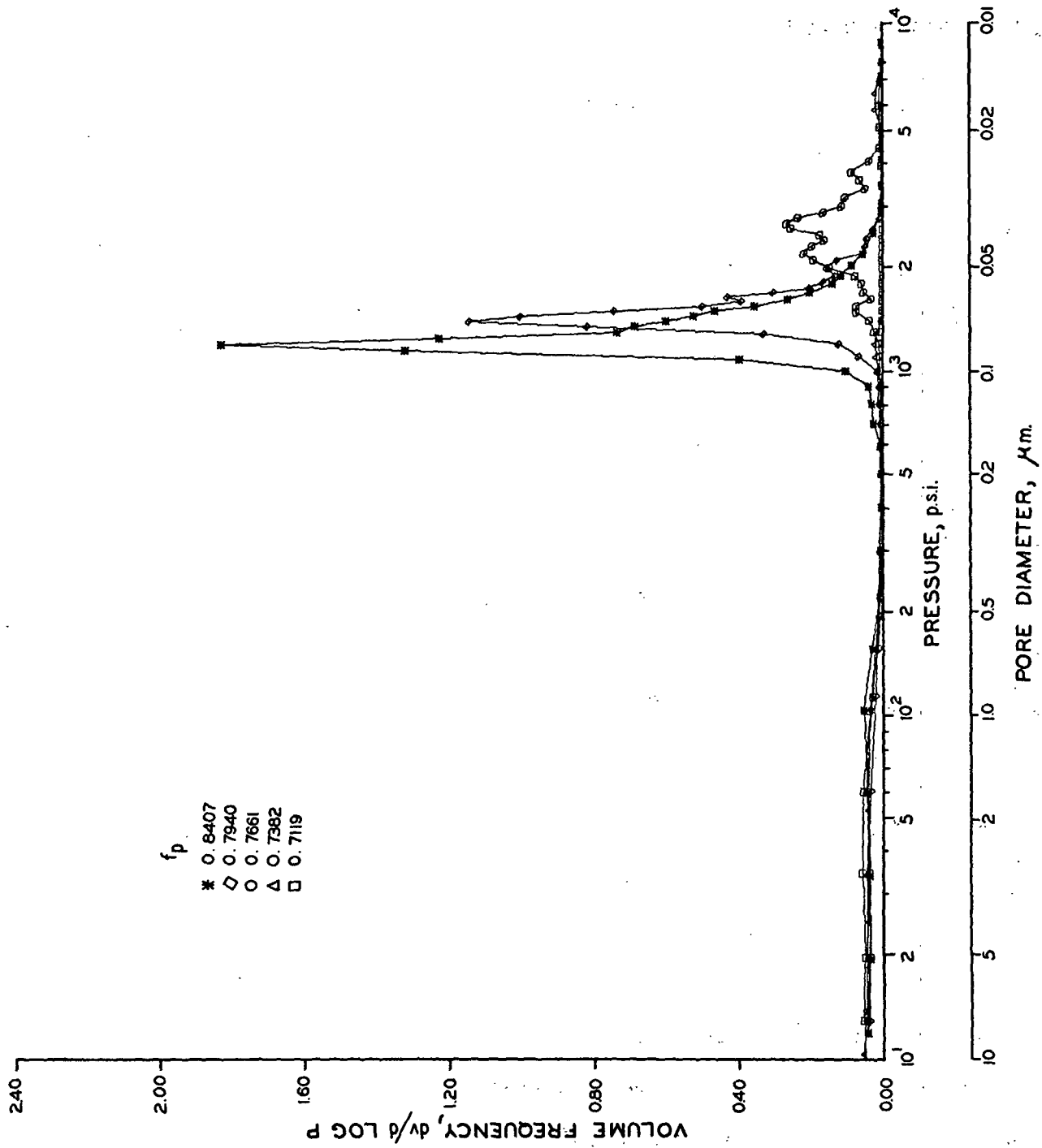


Figure 5. Volume Frequency vs. Pressure Distribution for the Compacting Structures of Type 2X Clay-Starch Coatings

Finally a starch level ($f_p = 0.82$ or 22 parts starch/100 parts clay) was reached at which there was a decrease in pore size and film volume.

CLAY-DEXTRIN STARCH COATINGS PREPARED BY BURKE

It was pointed out in the Experimental Procedures section that the techniques used by Burke (2) to determine the thickness of his coating samples resulted in an increase of 15% due to swelling of the sample in the embedding material. In the present study, the volume of the starch-clay coatings prepared by Burke were re-measured using the mercury porosimeter. The data are presented in Fig. 6 and are listed in Appendix II, Table IX.

The plot of the revised film volume data points for Burke's starch-clay coatings has the same general shape as the plot for Type 2X clay-starch coatings. There was an initial increase in film volume from 0.753 to 0.819 cc./g. clay, followed by a region in which the volume was constant. Finally, there was a decrease in film volume at high levels of starch. It should be noted that in the pigment films containing no adhesive, the film volume for Burke's clay was 0.753 cc./g. of clay while that for Type 2X clay was 0.653 cc./g. This is possibly due to the larger size of Burke's clay particles and a difference in the particle size distributions.

The volume frequency-pore size distribution curves for Burke's starch-clay coatings were also similar to those for Type 2X clay coating films. For Burke's starch-clay coatings there were no coating samples available for the region in which the volumes were expanding. Therefore, Fig. 7 shows the peak for the film with clay pigment alone while the rest of the peaks represent the region in which there was no change in film volume. There was a shift in the peaks of the frequency curves from 910 to 710 p.s.i. (0.11 to 0.14 μ m.). The position of the peaks in the volume frequency curves are given in Appendix IV, Table XIII. Figure 8 shows the volume frequency vs. pore size distribution curves for the region in which the film volumes

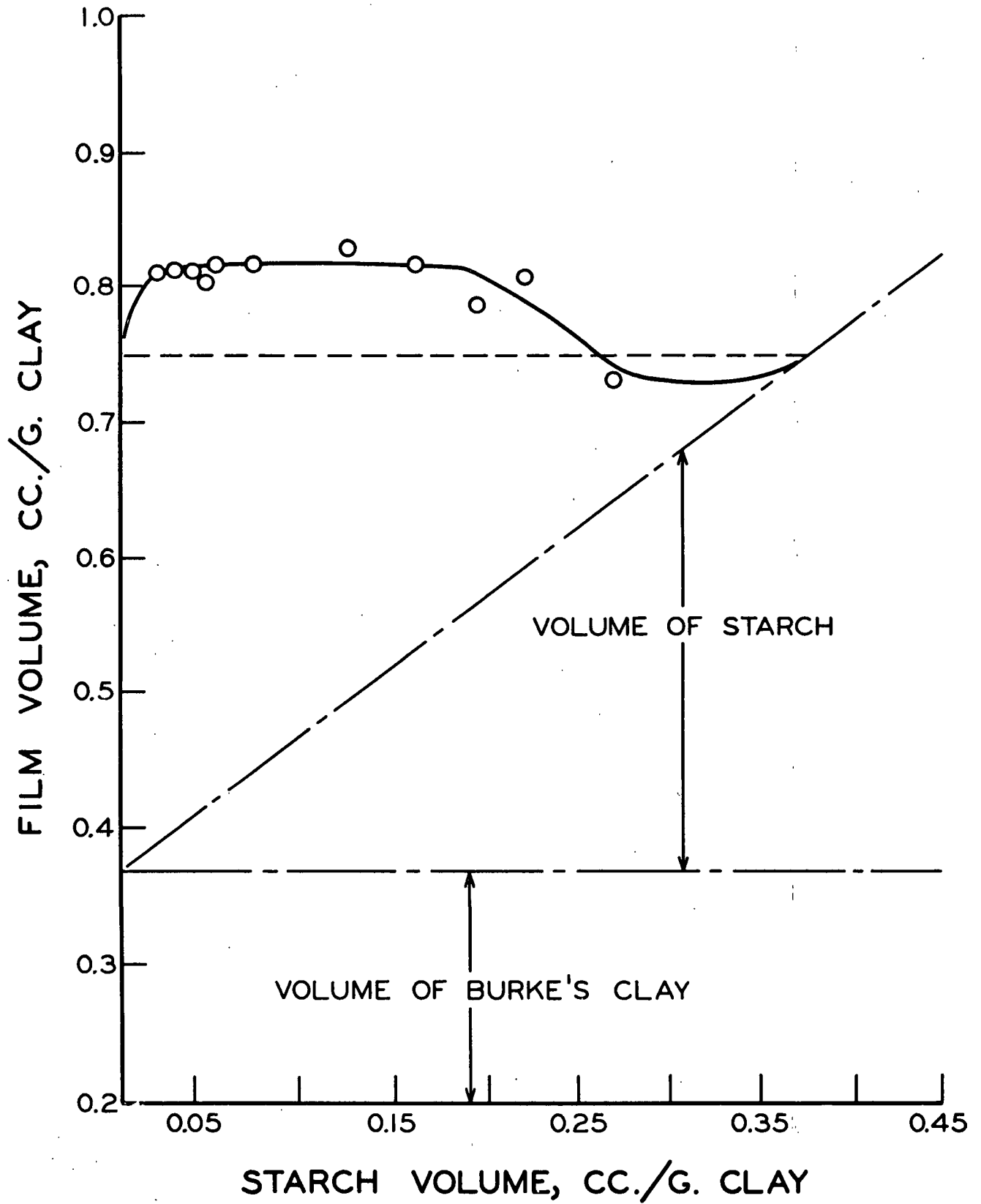


Figure 6. Changes in Film Volume per Gram of Clay vs. Changes in Adhesive Volume per Gram of Clay for Burke's Starch Clay Coatings

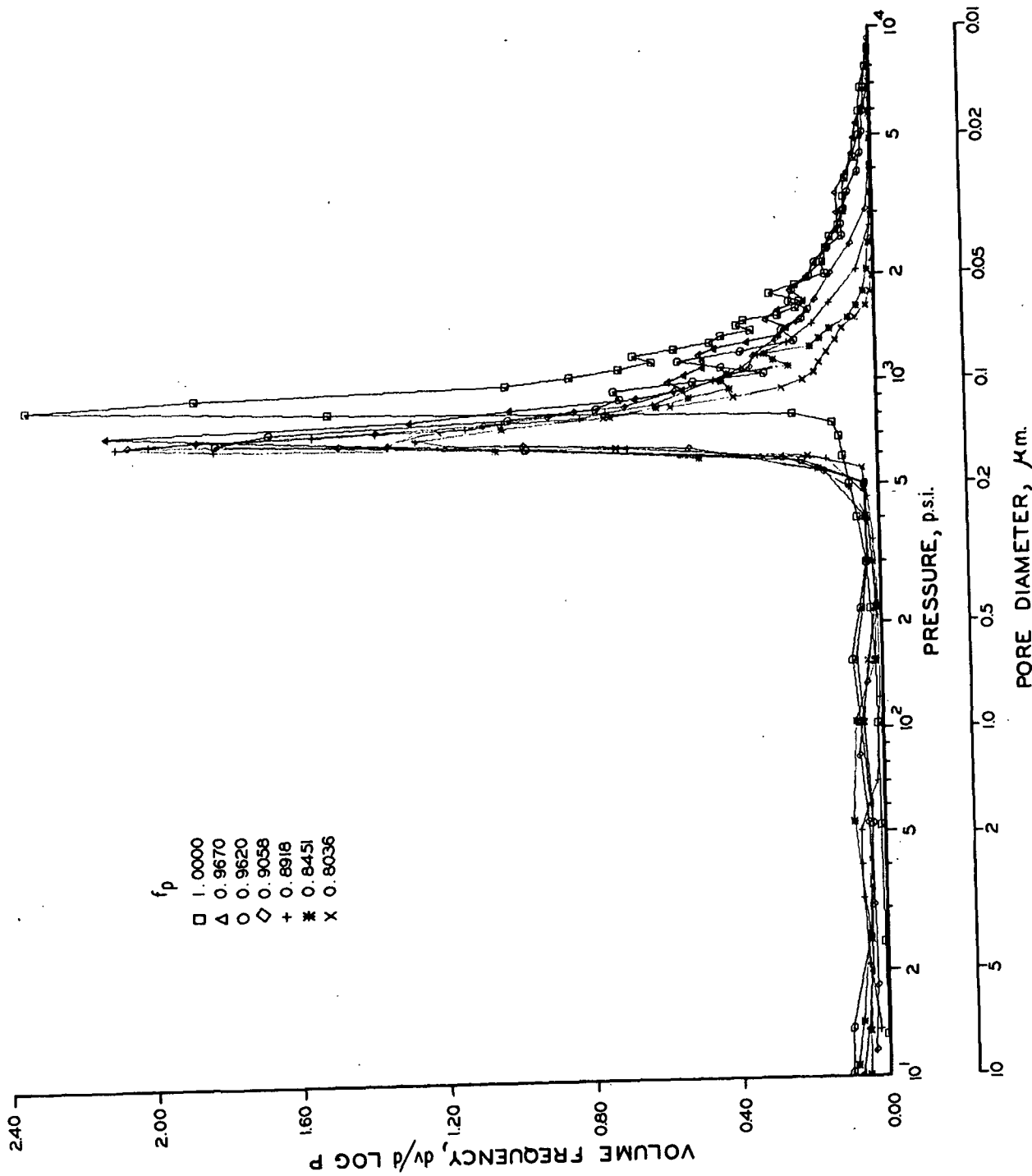


Figure 7. Volume Frequency vs. Pressure Distribution for the Constant Structures of Burke's Starch-Clay Coatings

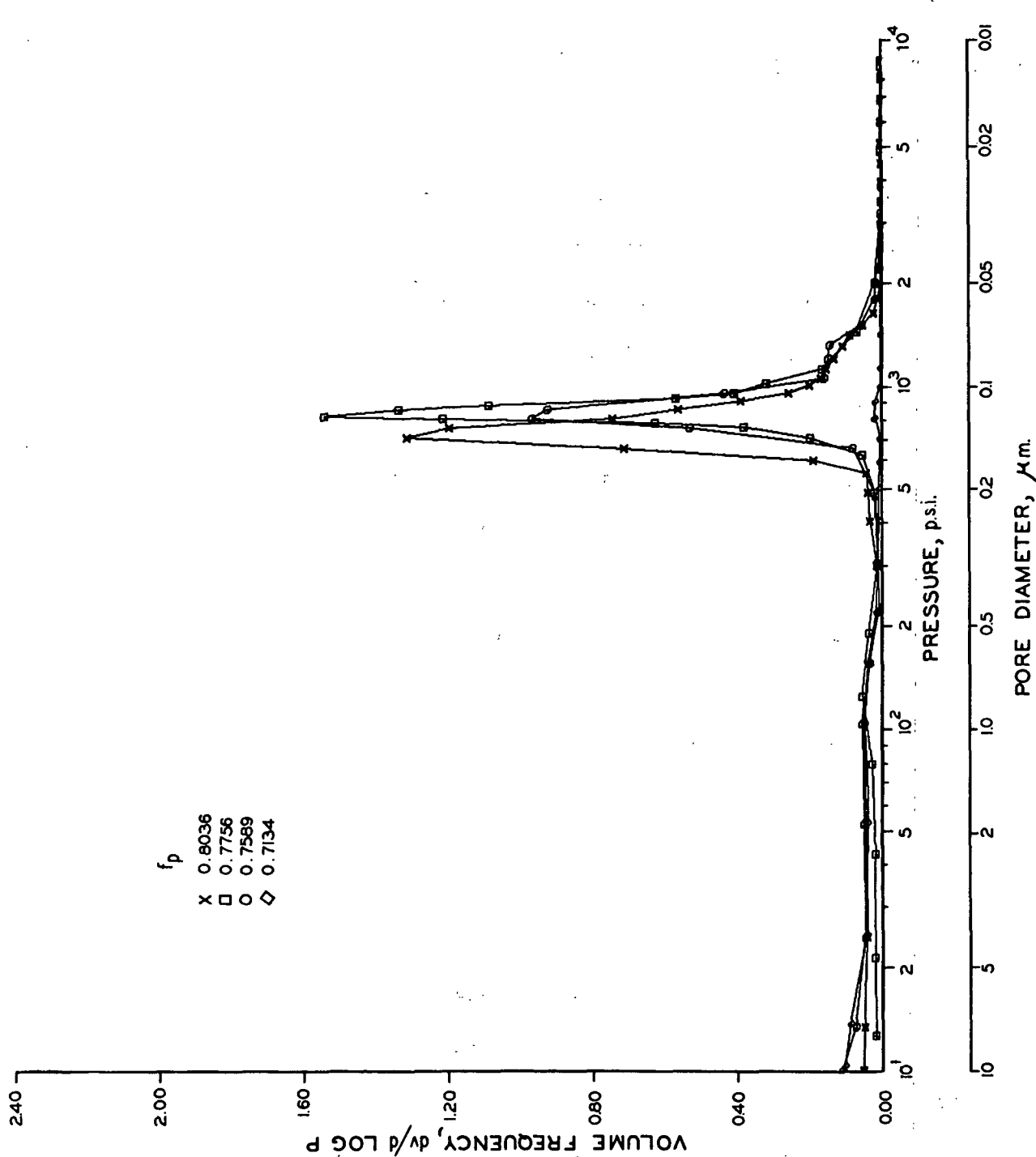


Figure 8. Volume Frequency vs. Pressure Distribution for the Compacting Structures of Burke's Starch-Clay Coatings

were decreasing. It is evident from these curves that the size of pores in Burke's starch-clay coatings were larger than those in corresponding Types 2X clay coatings. These larger pores are possibly due to the larger particle thickness of Burke's clay.

TYPE 2X CLAY-OXIDIZED STARCH COATINGS

Albrecht (28) conducted a study of the changes in structure of coatings prepared from Type 2X clay using Stayco M Starch (a sodium hypochlorite-oxidized cornstarch produced by the A. E. Staley Manufacturing Co.) as an adhesive. The techniques used in preparing and evaluating the coatings were identical to those in the present work. An oxidized starch was chosen because of its strong film-forming properties and its extensive use in the paper coating industry (29).

The film volume per gram of clay vs. starch volume per gram of Albrecht's clay plot is shown in Fig. 9 and the data are tabulated in Appendix IV, Table X. The curve drawn through the data points is almost identical to that obtained for the dextrin starch coatings. The increase in film volume was the same for both types of starches and also, the amount of shift in the size of pores, while not shown here, was equal for both types of starch coatings. Thus, both types of starch coatings behaved in the same manner even though the starches had been commercially modified differently.

TYPE 2X CLAY-POLYVINYL ALCOHOL COATINGS

A series of coating colors was prepared containing varying ratios of PVA and Type 2X clay. The film volume per gram of clay for these films is plotted vs. PVA volume per gram of clay in Fig. 10. The film volumes of the PVA-clay coatings increased with initial increments of PVA as did the starch-clay coatings. The film volume expanded from 0.65 to 0.72 cc./g. clay as compared to an expansion to 0.74 cc./g. clay for the starch-clay coatings. The maximum was reached at $\frac{f}{p} = 0.975$

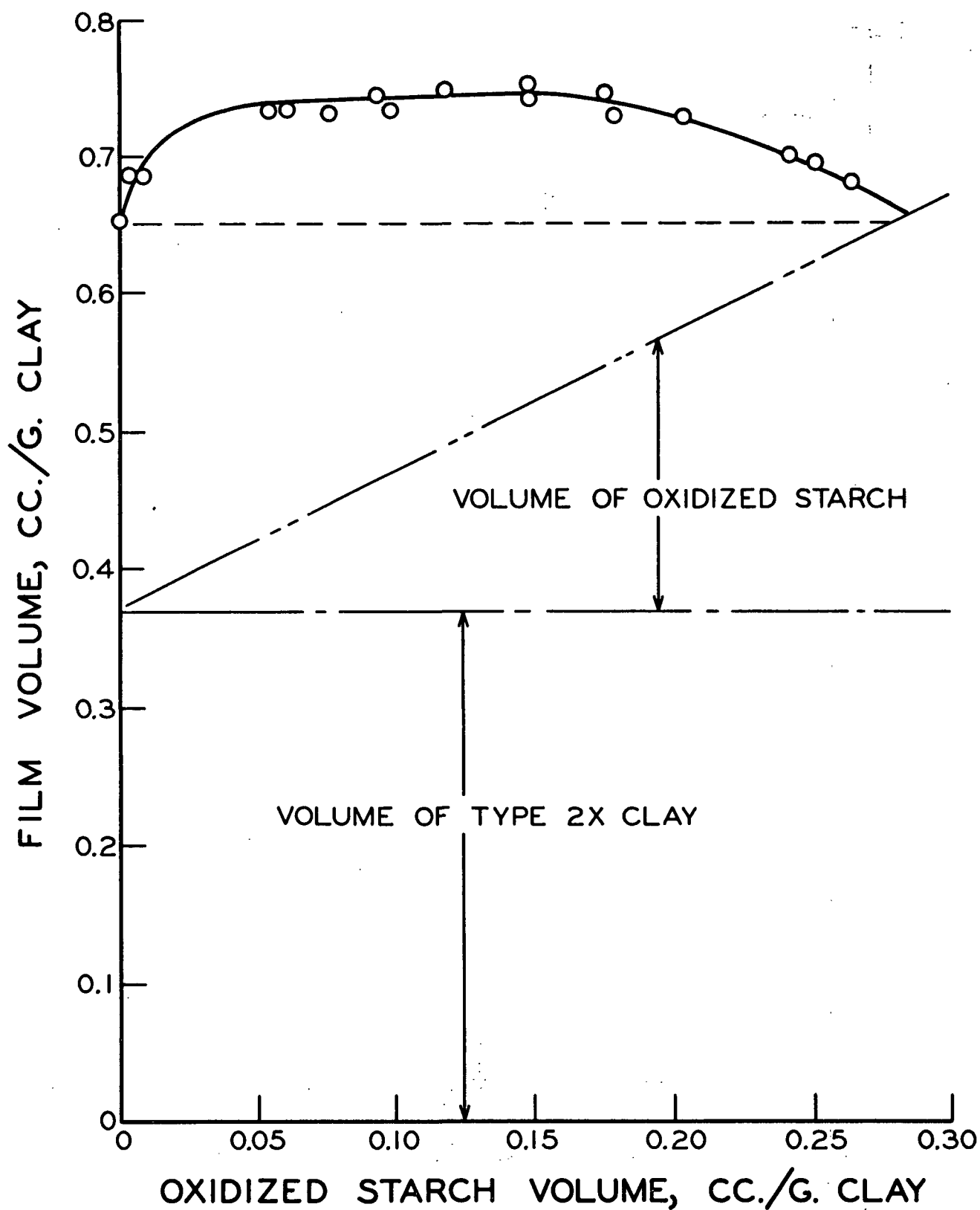


Figure 9. Changes in Film Volume per Gram of Clay vs. Changes in Starch Volume per Gram of Clay for Type 2X Clay-Oxidized Starch Coatings

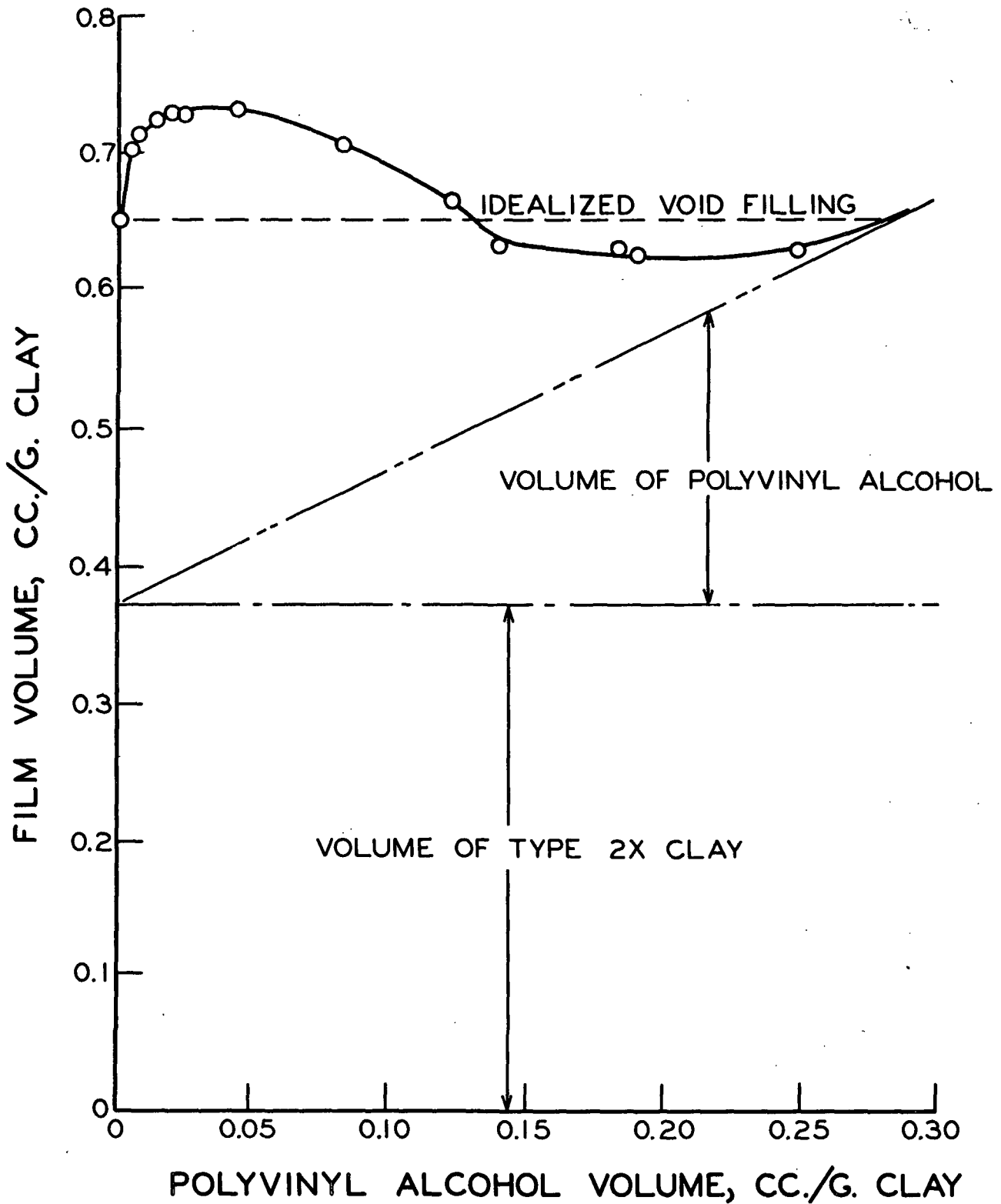


Figure 10. Changes in Film Volume per Gram of Clay vs. Changes in Polyvinyl Alcohol per Gram of Clay for Type 2X Coatings

(2.5 parts PVA/100 parts clay) as compared to $f_p = 0.960$ (4 parts starch/100 parts clay) for the starch-clay coatings. It is evident from Fig. 10 that the range of PVA concentrations over which the film volumes remained constant was significantly less than that for starch coatings (a $f_p = 0.975$ to 0.920 for PVA as compared to $f_p = 0.960$ to 0.820 for starch). The film volume decreased as the amount of PVA was further increased and actually fell below the line representing idealized void filling.

The volume frequency vs. pore size distribution curves for the PVA-clay films which were undergoing expansion were similar to the starch-clay coatings and are shown in Fig. 11. The shift in the peak of the frequency curves was from 1860 to 1410 p.s.i. (0.053 to 0.070 $\mu\text{m.}$) which was less than that for the starch-clay coatings. This indicated that the increase in pore size for PVA coatings was less than for starch coatings. The position of the peaks in the volume frequency curves is given in Appendix IV, Table XIII.

The volume frequency vs. pore size distribution curves for the region in which the PVA clay film volumes were constant is shown in Fig. 12 and for the decreasing film volumes in Fig. 13. These curves were similar to those for the starch-clay coatings except there was a smaller range of adhesive concentrations over which the film volumes remain constant. Compared to the starch system, there was less filling of small pores in the constant volume region before the film volumes started decreasing.

The foregoing results have shown that the film volumes of PVA-clay coatings increased as initial increments of PVA were added; however, the increase was not as great as for starch-clay coatings. The range of PVA concentrations over which the film volumes were constant was significantly less than for starch-clay coatings. In addition, the initial increase in pore size upon film expansion was less for the PVA-clay coatings than for the starch system.

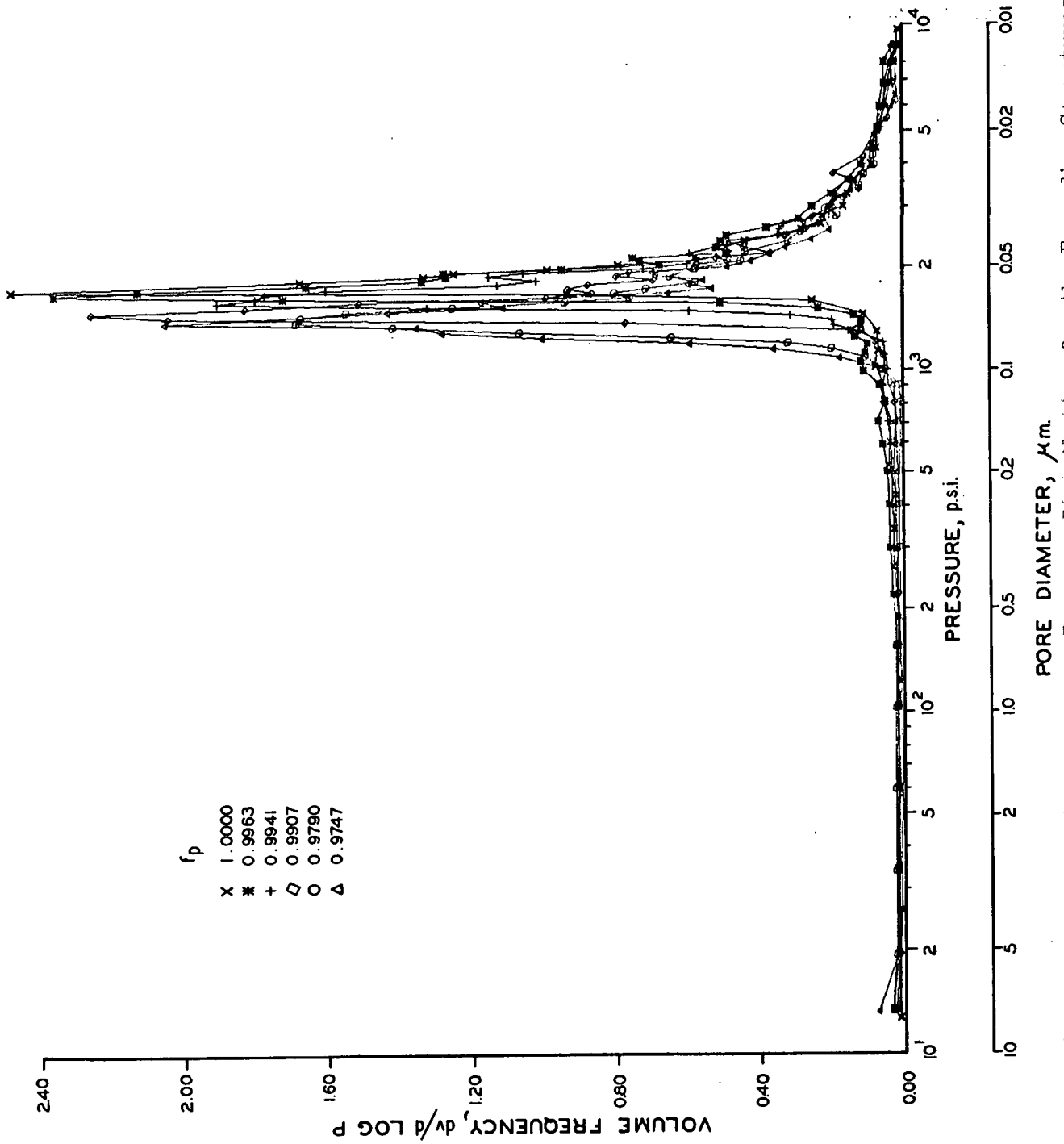


Figure 11. Volume Frequency vs. Pressure Distribution for the Expanding Structures of Type 2X Clay-PVA Coatings

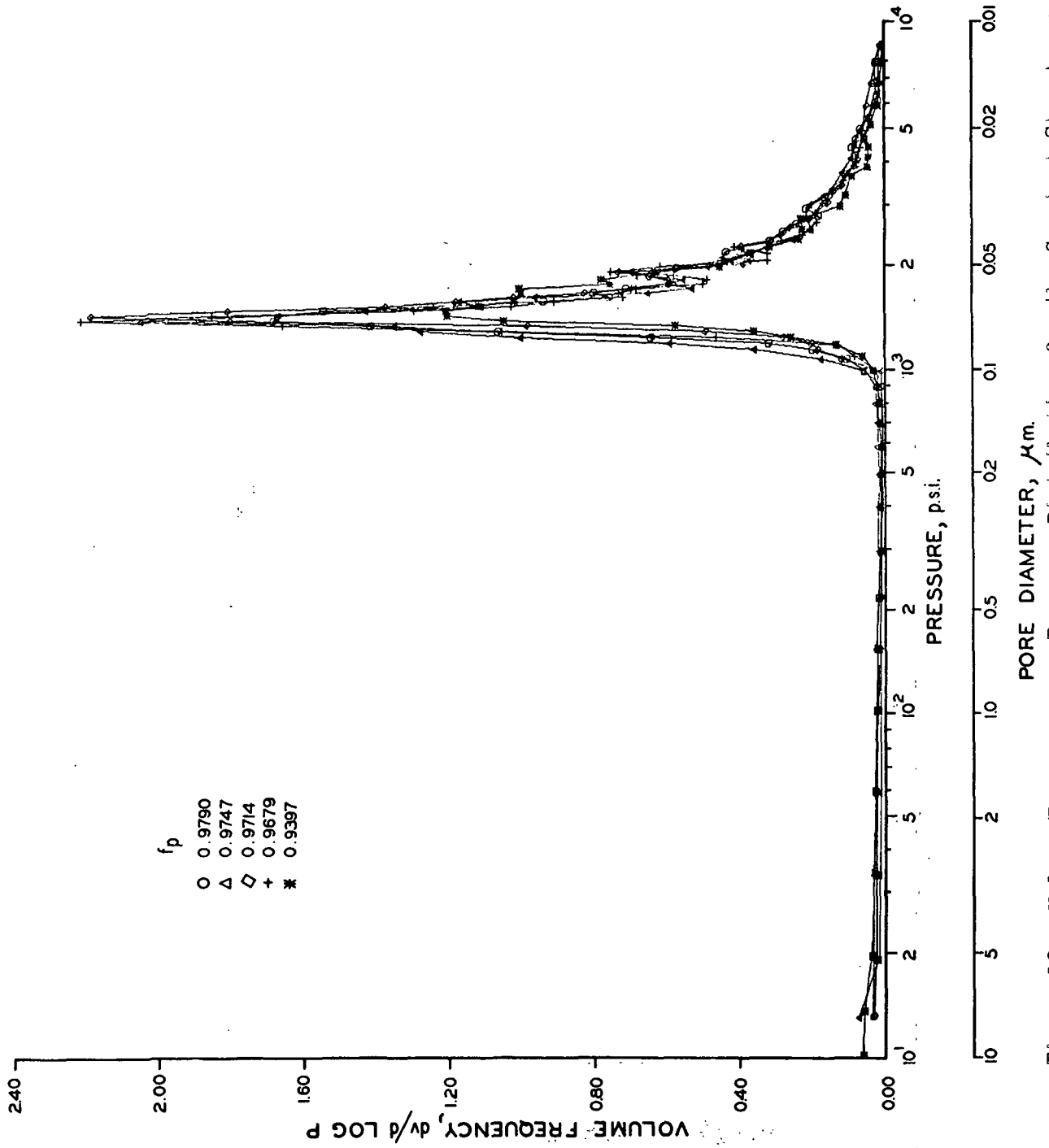


Figure 12. Volume Frequency vs. Pressure Distribution for the Constant Structures of Type 2X Clay-PVA Coatings

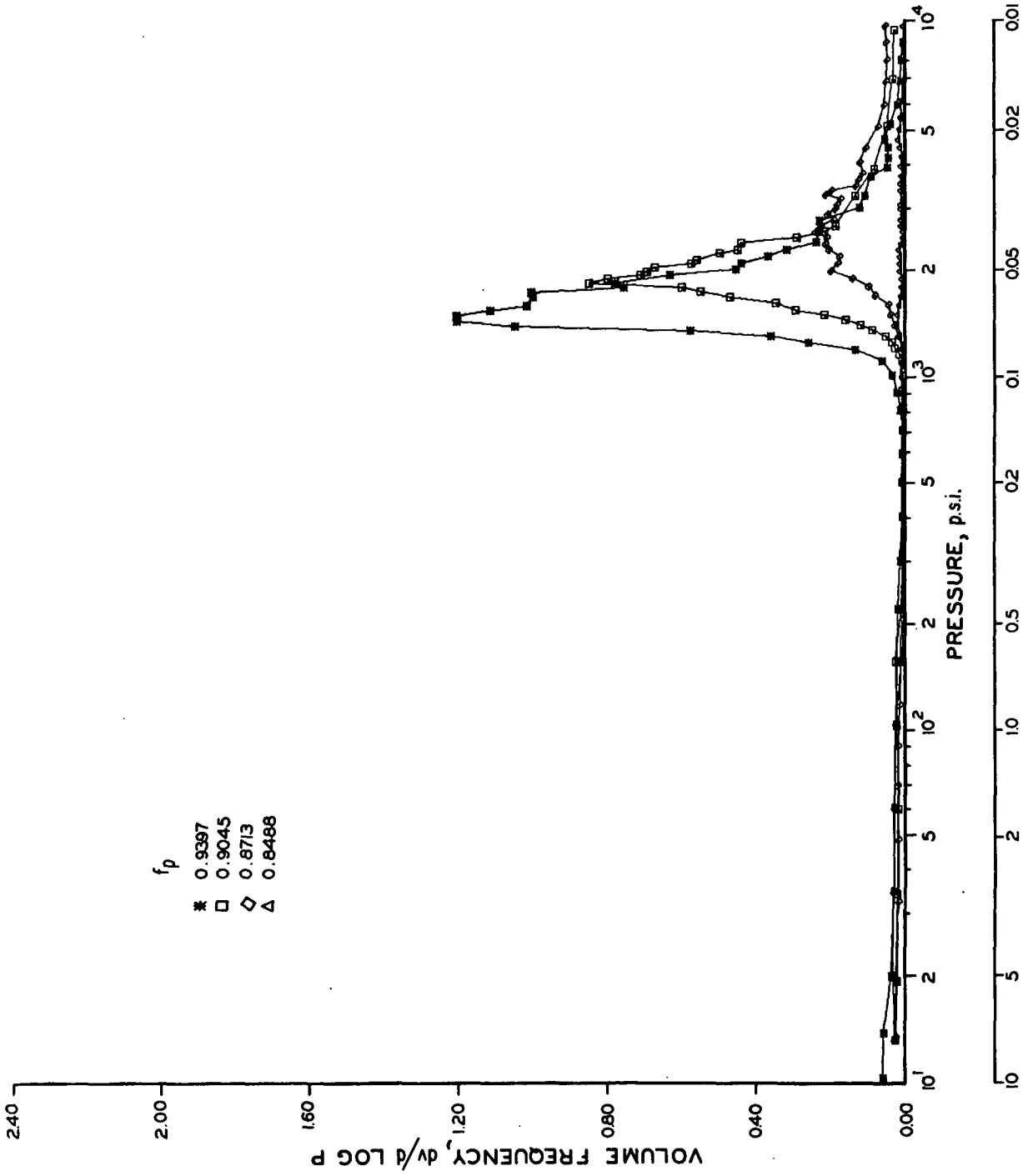


Figure 13. Volume Frequency vs. Pressure Distribution for the Compacting Structures of Type 2X Clay-PVA Coatings

SUMMARY OF THE CHANGES IN STRUCTURE OF CLAY COATINGS

The present study has characterized the changes which occurred in the overall as well as the internal structure of various clay coatings as a function of the level of adhesive present. The results of this study confirm Burke's observation that there is an interaction between the adhesive and clay pigment which influences the structural formation of the coatings.)

There were three distinct changes which occurred in the coating structure as the amount of adhesive was increased. The initial change, as the first increments of adhesive were added, was an increase in the film volume and a shift to a larger pore size. The initial increase was followed by a region in which the film volume and dominant pore size remained constant as the amount of adhesive was increased. The additional adhesive appeared only to fill the small pores without changing the structure. The range of adhesive contents over which there is essentially a constant pigment skeleton varies according to the type of adhesive used in preparing the coatings. The range of concentration of PVA films with constant volume was less than for dextrin or oxidized starches, which were approximately the same. The third change in the structure of the pigment films was a compaction in which the film volume decreased and the pore size distribution became narrower until all of the pores were filled with adhesive.

FLOCCULATION STUDIES

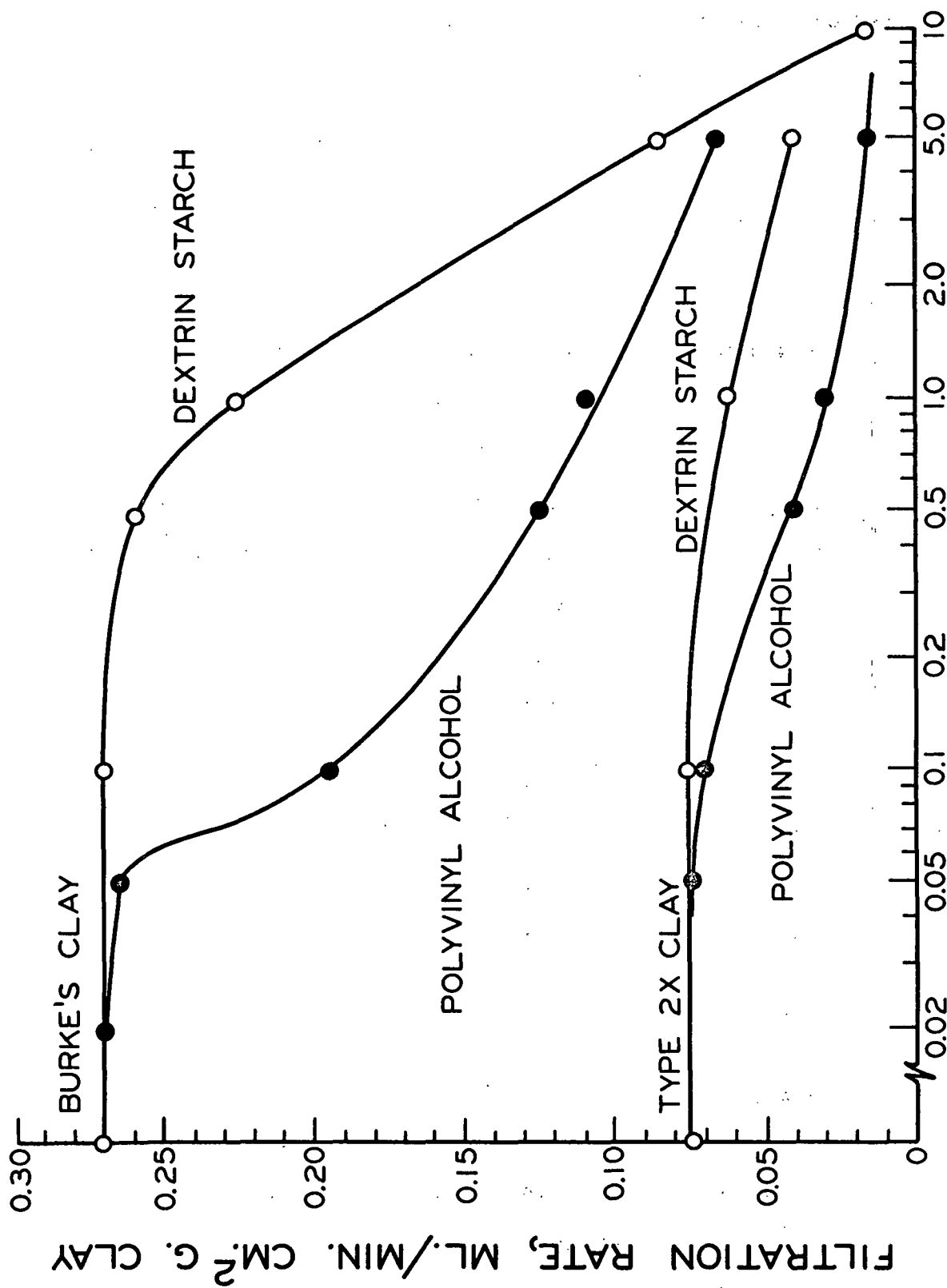
The work described in the previous section, confirmed earlier findings (2) that the level of adhesive plays a significant role in determining the structure of clay coatings. It was thus apparent that there was a definite and reproducible interaction occurring between the adhesive and clay pigments. As proposed earlier, this interaction was thought to be explained by a flocculation mechanism.

The flocculation hypothesis was investigated using a variety of experiments. Filtration rate studies were made of dilute coating colors to determine if flocculation was occurring by polymeric bridging. Low shear viscosity measurements were made of clay slurries in an adhesive diffusion study to determine if the binder had the ability to "rob" the dispersing agent from the clay and cause flocculation. Viscosity measurements to detect flocculation were made on coating colors at various levels of adhesive. Finally, measurements were made of possible changes in the size of the coating particles before and after the addition of an adhesive.

FILTRATION RATE STUDIES OF COATING COLORS

Determination of the filtration rates, made by passing the filtrate back through formed filter cakes of the coating materials, was the first technique used to detect possible flocculation. Such flocculation would result from polymeric bridging of the pigment particles as suggested by La Mer (15). If this type of flocculation was occurring, it was expected that the filtration rates would increase as the first increments of adhesives were added and eventually pass through a maximum. This maximum would indicate the adhesive level at which the largest floc size occurred. The results of the filtration rate studies for both PVA and starch with Type 2X clay are shown in Fig. 14 and the data are given in Appendix V, Table XV. Also shown are the results of filtration studies using Burke's clay with PVA and with starch.

It is evident from Fig. 14 that there was no increase but an actual decrease in filtration rates as a function of added adhesive for both starch and PVA. The filtration rates decreased more rapidly for PVA than starch. The initial filtration rate of Burke's clay was 3.8 times as great as that for Type 2X clay which indicates that Burke's clay formed a more porous filter cake. This is in agreement with the porosimeter measurements made on the clay pigment films which also showed Burke's clay to form more porous structures.



WEIGHT PERCENT POLYMER BASED ON CLAY

Figure 14. Filtration Rates for Type 2X Clay and Burke's Clay with Polyvinyl Alcohol and Dextrin Starch

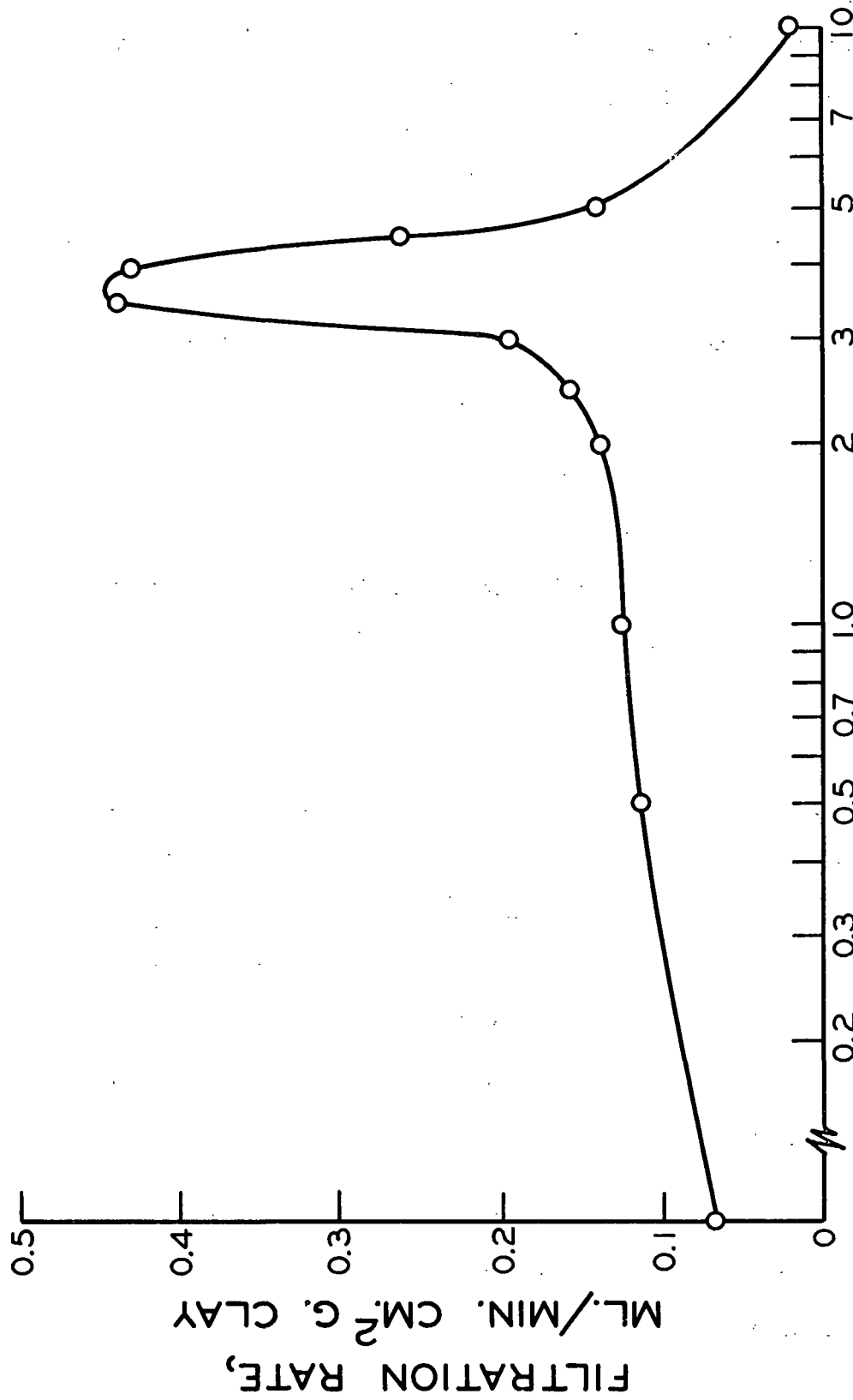
The filtration rates of a third pigment-polymer system were determined in order to confirm that the apparatus was properly constructed and techniques employed were correctly worked out. The pigment was Type 2X clay and the polymer was Cato 8 starch (a cationic starch produced by National Starch Company). The results of this filtration rate study are given in Fig. 15 and the data are listed in Appendix VI, Table XVII. In the study using Cato 8 starch, the filtration rates increased with added polymer and did pass through a maximum at approximately 4% starch based on the weight of the pigment.

La Mer (15) has shown that the pigment-polymer systems which exhibit the proposed polymeric bridging type of flocculation conform to what is called the eighth power filtration law. According to this theory if $\ln (\frac{P_m}{P_o} + \frac{P_o}{Q})$ is plotted vs. $\ln (\frac{P_o^4}{[Q - Q_o]})$, the slope should be equal to 8.0. $\frac{P_m}{P_o}$ is the concentration of the polymer at the maximum filtration rate, $\frac{P_o}{P_o}$ is the concentration of the polymer in the suspension being filtered, $\frac{Q}{Q}$ is the filtration rate of the suspension being filtered, and $\frac{Q_o}{Q_o}$ is the filtration rate of the suspension containing no polymer. The slope of this plot for the Cato 8 starch-clay system was equal to 8.1.

The Cato 8 starch-clay filtration rate studies showed that the polymeric bridging type of flocculation described by La Mer can be detected in a kaolin clay system if the right polymer is selected. However, the pigment-adhesive systems used in the coating study of this thesis do not appear to exhibit this type of flocculation.

ADHESIVE DIFFUSION STUDY

When clay is dispersed in water, various materials such as dispersing agent and NaOH are added to stabilize the suspensions. An investigation was carried out to determine if the adhesive was "robbing" the dispersing agent from the clay, thus causing it to flocculate. A clay slurry was separated from the solutions of adhesive by a viscose membrane. A low-shear capillary viscometer was used to detect if



WEIGHT PERCENT POLYMER BASED ON CLAY

Figure 15. Filtration Rates for Type 2X Clay-Cato 8 Suspensions

flocculation was occurring by measuring the time necessary for a given volume of the clay slurry to pass through a capillary connecting two graduated cylinders. The results of the studies for both PVA and starch are shown in Fig. 16 and the data are listed in Appendix VI, Table XIX.

The solid line in Fig. 16 represents the viscosity of the clay slip as a function of solids content. If the only action of the adhesive is to imbibe water from the clay, the viscosities should fall on this line. However, if the adhesive "robs" the dispersing agent from the clay and causes flocculation, the viscosities will be above the line representing the change in viscosity vs. change in solids content.

The results shown in Fig. 16 indicate that the only function of the adhesive was to imbibe water from the clay thus increasing the viscosity of the clay slurry. There was no indication that the clay was undergoing flocculation.

VISCOSITY MEASUREMENTS OF COATING COLORS

The low shear capillary viscometer was used to measure the viscosity of a series of starch-clay colors. The purpose of this study was to determine if there was any abrupt change in viscosity of the coating colors as a function of starch content which could indicate the onset of flocculation. The range of starch concentrations used covered the region in which the coating structures underwent expansion. The results of the viscosity measurements are shown in Fig. 17 and the data are listed in Appendix VII, Table XX.

The viscosity of the coating colors increased as the amount of starch was increased. No abrupt viscosity change was observed which could have been interpreted as flocculation.

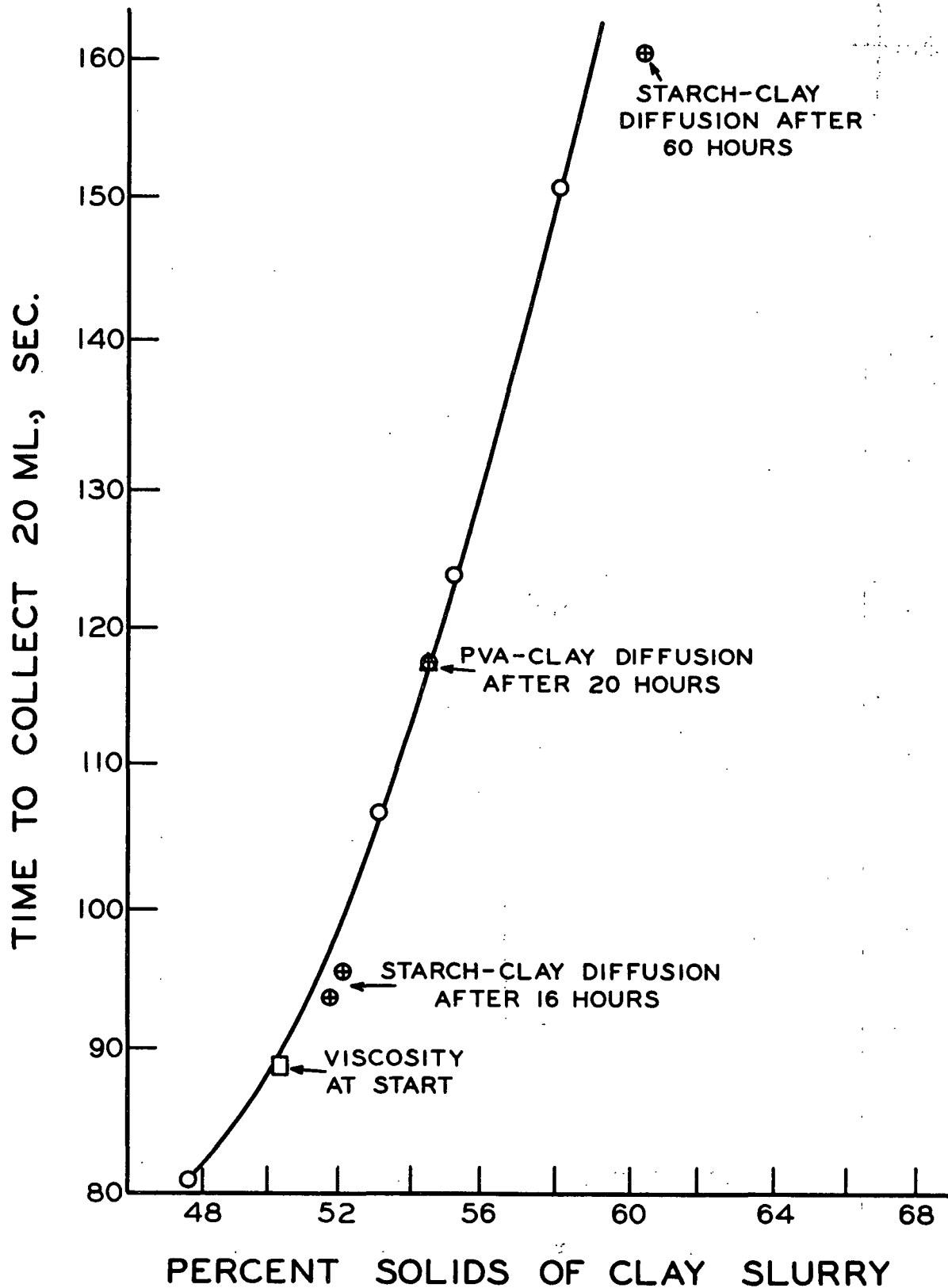


Figure 16. Low Shear Viscosity Measurements of Clay Slurries in Adhesive Diffusion Study

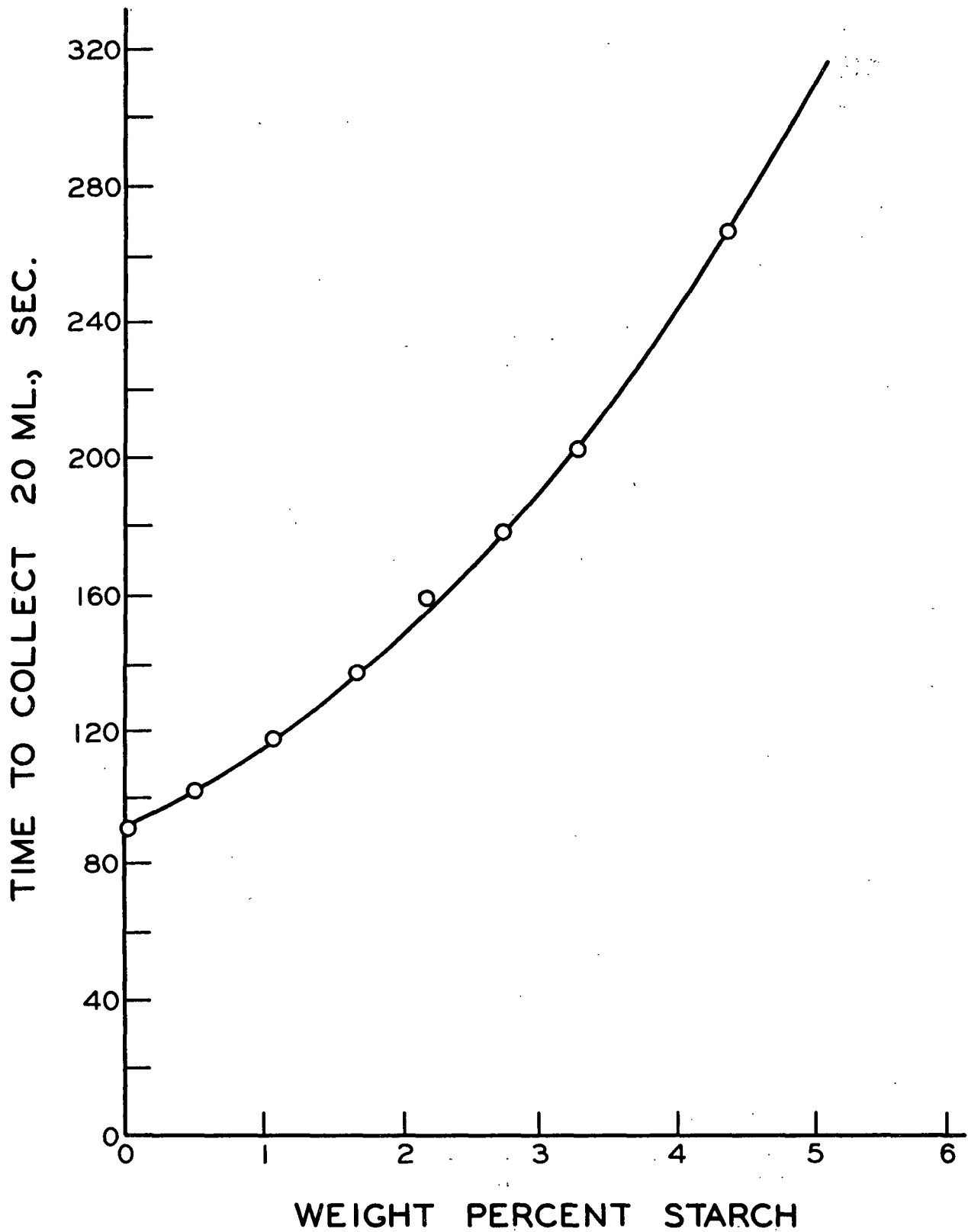


Figure 17. Low Shear Viscosity Measurements of Type 2X Clay-Starch Coating Colors

HIGH SHEAR MIXING OF COATING COLORS

It was believed that any flocs present in the coating colors would be broken up by high shear mixing. A starch-clay coating color was prepared at $\frac{f}{p} = 0.94$ (7 parts starch/100 parts clay) and divided into two portions. One portion was applied to the tinfoil in the normal manner. The other portion was mixed in a high shear Eppenbach Homo mixer for 30 minutes before forming the film on tinfoil. A comparison of the film volumes and pore size distribution showed that the high shear mixing did not change the structure of the coatings.

PARTICLE SIZE MEASUREMENTS OF COATING COLORS

An attempt was made to detect flocculation by determining if there was a change in the size of the coating particles before and after the addition of an adhesive. The Coulter Counter (16) and optical microscope were used to measure the size of the coating particles. The results of the Coulter Counter measurements are shown in Fig. 18 and the data are listed in Appendix VII, Table XXI.

There did not appear to be any significant change in the particle size distributions when samples were compared before and after the addition of PVA or starch. If flocculation had occurred, it would be expected that the particle size would at least double or triple. This was not observed. Flocculation could be detected when the particles were permitted to stand for 15 minutes in the 1% NaCl solution used in making the Coulter Counter measurements. It was observed that the particles in the coating colors, which had been in contact with PVA and starch, were more stable in the 1% solution than the clay pigment particles without adhesive. This is expected because of the protective colloidal nature of the polymer.

The clay particles were visible under the oil immersion lens of an optical microscope. It was not possible to detect any change in particle size when comparing

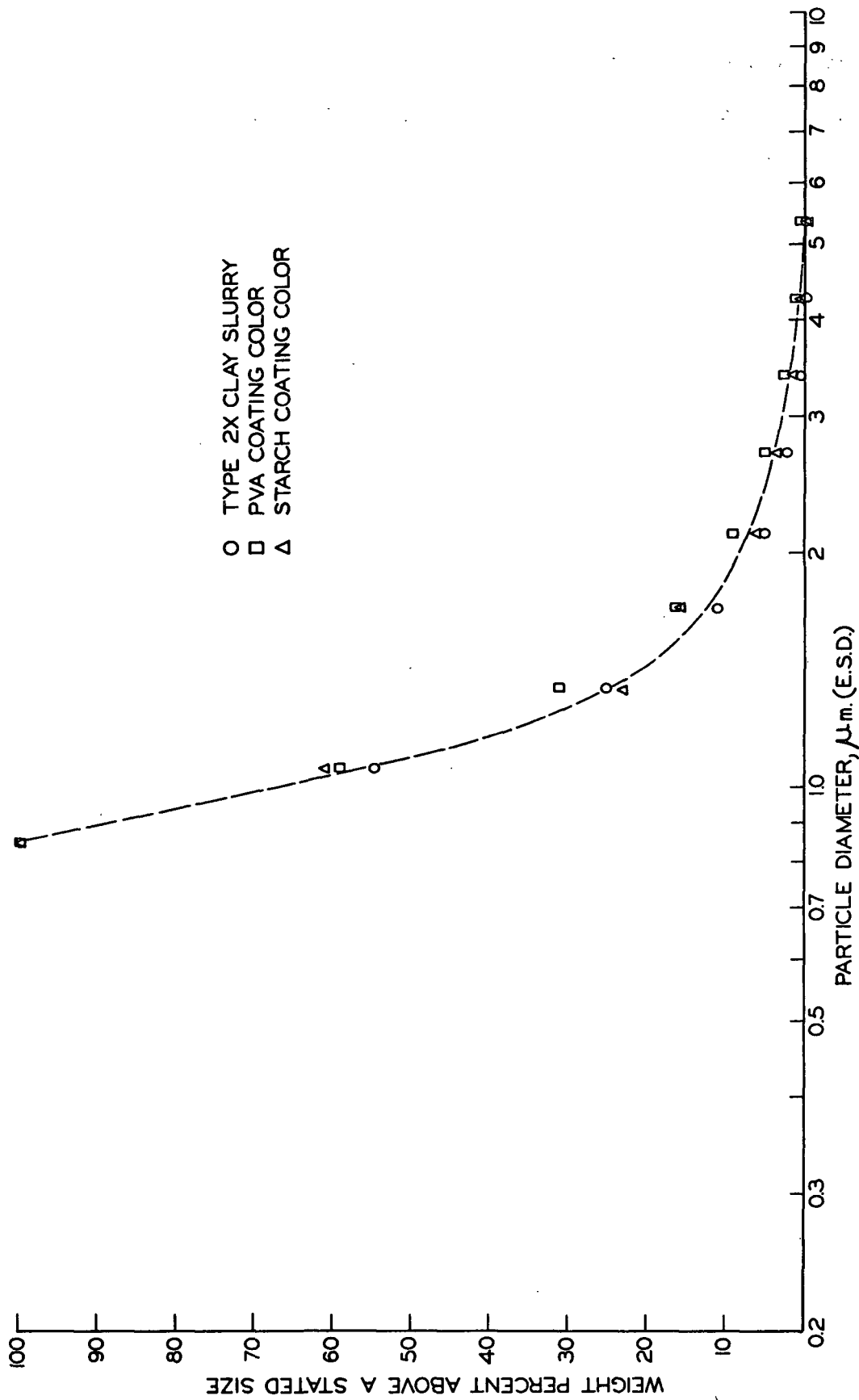


Figure 18. Coulter Counter Measurements of Type 2X Clay Coating Colors

samples before and after the addition of an adhesive. Floccs were seen when a drop of 1% NaCl solution was added to the clay particles, with no adhesive present. However, no floccs were detected in the coating colors themselves.

SUMMARY AND CONCLUSION OF THE FLOCCULATION STUDIES.

A flocculation phenomenon was originally considered as a possible mechanism for the changes observed in the coating structure. The flocculation studies carried out in this thesis, including filtration rate, viscosity, and direct particle size measurements, showed that no flocculation was occurring. It was therefore concluded that flocculation was not responsible for the structural changes which were observed in the clay coating.

CHANGES IN THE SURFACE TENSION OF COATING COLORS

An investigation was made of the effect of the reduction in surface tension on the packing characteristics of pigment particles with increasing levels of adhesive. This reduction could possibly lead to a less dense packing of the pigment particles and an expanded film volume.

The surface tension of the coating colors was measured as a function of the amount of adhesive present and the results are shown in Fig. 19. The data are listed in Appendix VII, Table XXII. There was a greater decrease in surface tension for the starch-clay colors than for the PVA-clay coating colors. However, the decrease in both systems was gradual and the values of the surface tension did not become constant until a high concentration of adhesive was reached ($\frac{f_p}{p} = 0.83$ or 25 parts adhesive/100 parts clay). The initial increase in coating film volume occurred at $\frac{f_p}{p} = 0.96$ and 0.975 (4 and 2.5 parts adhesive/100 parts clay) for starch and PVA. Little change had occurred in surface tension in this range of adhesive concentrations as noted in Fig. 19.

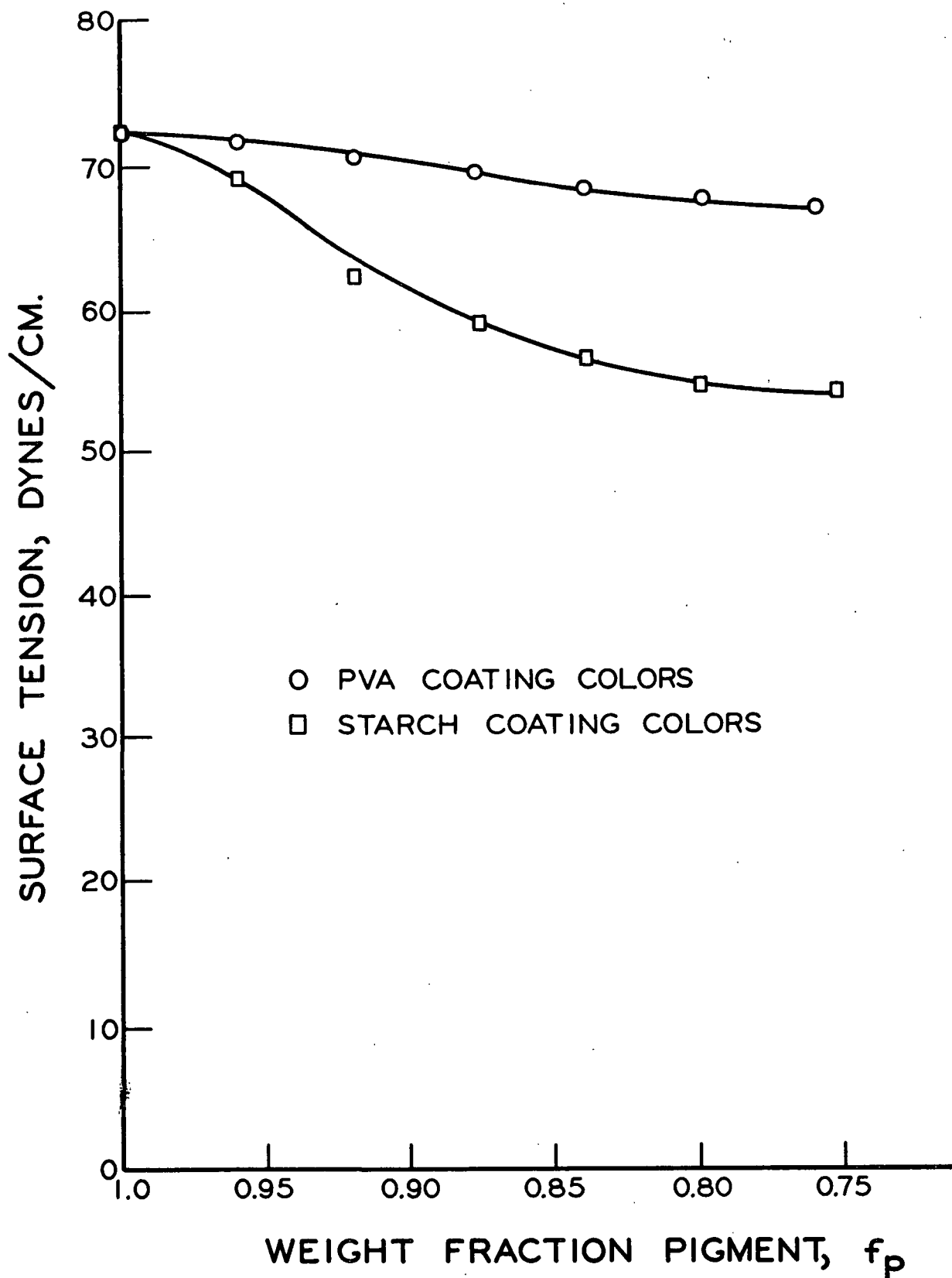


Figure 19. Change in Surface Tension of Coating Colors vs. Adhesive Content

In another test of the surface tension hypothesis, Triton X100 (a surfactant produced by the Rohm & Haas Co.) was added to a clay slurry to reduce its surface tension from 72 to 43 dynes/cm. This value of the surface tension was lower than those observed for the coating colors. Coating films were made from a clay slurry before and after addition of the Triton X100. The film volumes and pore size distributions for these films were found to be equivalent. This result indicated that the surface tension can be lowered to the level reached in these experiments and not change the packing characteristics of clay pigment particles.

PARTICLE ENCAPSULATION

The concept of particle encapsulation by a binder is based on the assumption that the adsorption of adhesive onto the clay pigment substrate takes place. Emery (30) indicated that relatively little quantitative work has been done in the area of polymer sorption. Even less work had been reported for systems such as the starch-clay and PVA-clay in which hydrogen bonding may occur. However, it has been shown qualitatively in many instances that polymers are adsorbed onto appropriate substrates. Kohl and Taylor (31) have shown that polymers are sorbed onto and hydrogen bonded to bentonite clays. Studies on the use of gum polymers as retention aids for paper fillers are based on the adsorption of the gums onto pigment surfaces (32). Michaels (33) discusses the adsorption of starch onto kaolin clay particles and subsequently hydrogen bonding. Based on the work reported in the literature, the assumption is reasonable that starch and PVA adsorption takes place in the systems considered here.

The effective particle size of a pigment is increased when an adhesive material is adsorbed on the surface of the pigment. These encapsulated or coated particles would tend to pack in a less dense manner due to the layers of adhesive separating the pigment particles. In testing this mechanism, it was necessary to determine

if the change in particle thickness due to the adsorbed adhesive was great enough to account for the observed increase in coating film volume. It was expected that if particle encapsulation was occurring the thickness of the adsorbed layer of adhesive would be the same on different sized clay platelets. Therefore, coatings made from larger clay particles would be expected to exhibit less increase in film volume because the relative increase in particle size is less.

When considering how changes in particle size could affect the film volume, it is helpful to visualize the arrangement of the clay platelets in the coating film. The clay particles have been shown to be preferentially oriented with their flat surface parallel to the plane of the surface of the substrate (2, 4). Such an arrangement of particles is shown schematically in Fig. 20 and in a cross sectional view in Fig. 21.

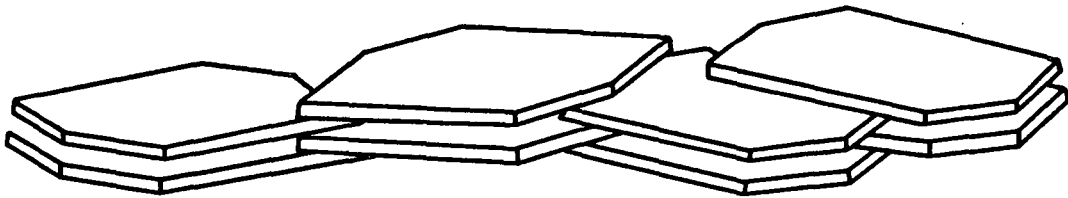


Figure 20. Arrangement of Clay Platelets in a Coating Film

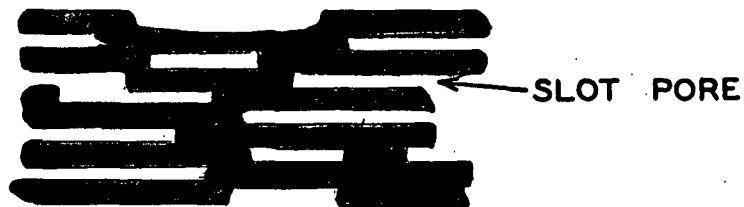


Figure 21. Cross Section of a Clay Coating Film

It can be seen from Fig. 21 that if the clay particles are well dispersed and pack in the described manner the pores in a coating film are of the slot form. Equation (2), which describes the pressure required to intrude mercury into a slot pore, can be expressed in terms of the width of the slot, \underline{D} , as,

$$D = \frac{2\gamma \cos\theta}{P} \quad (3)$$

when $\gamma = 475$ dynes/cm., $\theta = 155^\circ$, \underline{P} is expressed in p.s.i., and \underline{D} is in $\mu\text{m.}$,

Equation (3) becomes

$$D = \frac{98.8}{P} \quad (4)$$

The contact angle was assumed to be 155° based on the measurements described in the Experimental Procedures Section of this thesis.

It is evident from Fig. 21 that the size of the slots are equal to the thickness of the clay platelets. The size of the "number average slot width" was calculated for coating films without adhesive present to see if it was valid to use Equation (4) to describe the pores in a coating film. This diameter was compared to the thickness of the clay particles determined from the electron micrographs. The "number average slot width" was the method chosen to present pore size information obtained from the porosimeter data instead of comparing the peaks of the frequency curves. This was done because the shape of the frequency curves was unsymmetrical and the peaks did not represent an average pressure from which an average pore size could be calculated.

The "number average slot width" was calculated from the porosimeter data using Equation (4) to determine the pressures which corresponded to a series of slot widths that increased in size by equal increments of $0.004 \mu\text{m.}$ for Type 2X clay and $0.008 \mu\text{m.}$ for Burke's clay. This series of slot widths covered the range of pressure under the frequency curves for the coating films (i.e., 1,000 to 10,000 p.s.i. for

Type 2X clay coatings). The volume of mercury which entered into each increment of slot width was determined from the cumulative volume vs. pressure distribution curve. To determine the number of pores of each incremental size, it was necessary to assume a shape and size of the pore. The shape was assumed to be square and the dimensions are shown in Fig. 22.

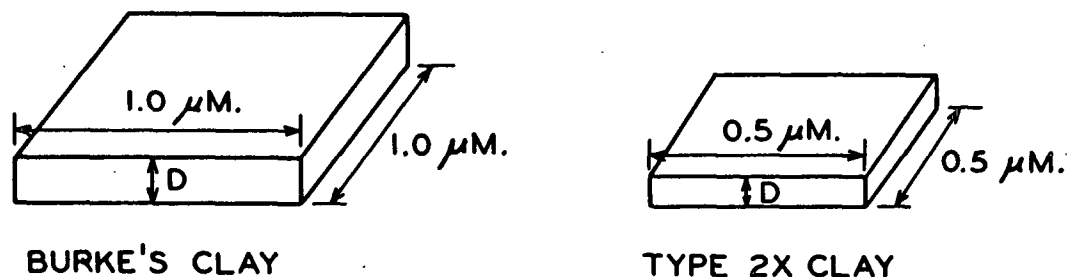


Figure 22. Assumed Size and Shape of Pores in Coating Films

The dimension for the base of each pore was chosen from the average length of the clay particles determined from the electron micrographs (see Table I). The size of the base was held constant and the width, D , was varied. This permitted the calculation of an average volume of one pore for each incremental size. Thus, knowing the average volume of one pore for each increment and the total volume of all pores of that size, it was possible to calculate the number of pores for each incremental size. An example of such a calculation is shown in Appendix VIII, Table XXIII. The number average slot widths were calculated from these distributions and are given in Table III.

The slot widths determined using Equation (4) and the particle thickness measurements from the electron micrograph agreed closely. If the equation for ideal cylindrical pores, Equation (1), had been used instead of Equation (4), the value of the average slot width for Type 2X clay would have been 0.084 μm. and 0.148 μm.

for Burke's clay. It is obvious that cylindrical pore values do not agree with the particle dimensions obtained from the electron micrographs. Therefore, Equation (4) was used to calculate the size of pores in the coating films reported in this study.

TABLE III
COMPARISON OF PARTICLE THICKNESS VALUES DETERMINED BY
POROSIMETER AND ELECTRON MICROGRAPHS

	Values of Number Average Slot Width, Equation (4), $\mu\text{m.}$	Value of Number Average Particle Thickness from Electron Micrograph, $\mu\text{m.}$
Type 2X clay	0.042	0.049
Burke's clay	0.074	0.088

Figure 23 shows how the encapsulation of pigment particles by a layer of adhesive increases the film volume. It is possible for the particles to be separated by one or two layers of adhesive. If two particles come together and have only one layer of adhesive between them, there will be an increase in the film volume but not in the pore size as shown in Fig. 23C. However, if there are two layers of adhesive between the pigment particles, the pore size as well as the film volume increases as illustrated in Fig. 23B.

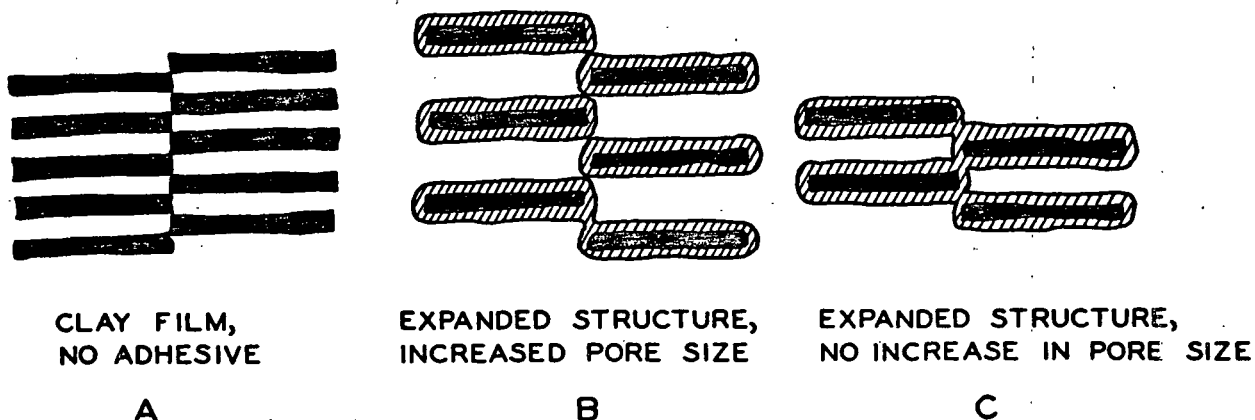


Figure 23. Idealized Model of the Structure of a Coating

The porosimeter data obtained in evaluating the coating structures indicated that there was an increase in pore size as well as in film volume when an adhesive was added to the clay pigment. Therefore, it is proposed the coating film expansion observed in this study occurred according to the mechanism pictured in Fig. 23B (i.e., where two layers of adhesive separate the pigment particles).

It is possible to calculate the thickness of the adsorbed layer of adhesive from the porosimeter data by determining the change in the average slot diameter. The number average pore width was calculated using Equation (4) for the coating films at the adhesive level where the maximum in film volume was initially reached. The results are given in Table IV and are compared to the pore diameters of the clay films without adhesive present. The frequency diagrams of the pore diameters determined in Table IV are given in Appendix X.

TABLE IV
THICKNESS OF ADSORBED ADHESIVE LAYER ON CLAY PIGMENTS
MEASURED BY MERCURY POROSIMETER

Coating Film	Number Average Pore Width, μm .	Thickness of Adsorbed Adhesive Layer, μm .
Type 2X clay - no adhesive	0.0421	--
Type 2X clay - starch coating, $f_p = 0.960$	0.0538	0.0058
Type 2X clay - PVA coating, $f_p = 0.975$	0.0514	0.0047
Burke's clay - no adhesive	0.0745	--
Burke's clay - starch coating, $f_p = 0.967$	0.0847	0.0050

The results in Table IV indicated that the thickness of the adsorbed layer of starch was the same for both Type 2X clay and Burke's clay, even though the thickness of the clay particles differed by a factor of approximately two. This result

meant that the effect of particle encapsulation on the expansion of coating film volumes would be less for thicker clay particles, which is what would be expected if the particle encapsulation mechanism was occurring.

A second method of calculating the thickness of the adsorbed adhesive layer involved measuring the increase in film volume between the line representing idealized void filling and the curve of data points in the region where expanded film volumes remained constant in Fig. 2. The change in coating film thickness necessary to account for the measured increase in film volume was determined by assigning dimensions to the particles of the model shown in Fig. 23. The dimensions of the clay platelets were taken from Table I. The void volume of clay films containing no adhesive was approximately 50% for Burke's clay and 43% for Type 2X clay. The model in Fig. 23 can be adjusted for the different void volumes by changing the amount of overlap of the clay platelets at the points of contact. As previously mentioned, this difference in void volume was probably due to the variation in particle size and particle size distribution between the two types of clay.

A sample calculation for determining the thickness of the adhesive layer from the change in film volume is given in Appendix XI. The calculated value for the thickness of the adhesive film separating the pigment particles was equal to twice the thickness of the adsorbed adhesive layer on each platelet. The values for the thickness of the adhesive layers determined from the changes in overall film volume are listed in Table V and are compared to those determined from the porosimeter data.

There was close agreement between the two types of measurements even though the thickness of the adhesive layers determined from the changes in film volume were somewhat less than those calculated from the porosimeter data. The adhesive film thickness determined by averaging the two methods was approximately 39 Å. for PVA and 47 Å. for dextrinized starch.

TABLE V

COMPARISON OF METHODS FOR DETERMINING THICKNESS
OF ADSORBED ADHESIVE LAYER

Coating Film	Thickness of Adhesive Layer Film Volume Measurements, μm .	Determined from Porosimeter Data, μm .
Type 2X clay - PVA coating	0.0030	0.0047
Type 2X clay - starch coating	0.0039	0.0058
Burke's clay - starch coatings	0.0035	0.0050

As previously mentioned, little or no information is given in the literature regarding the thickness of adsorbed layers of these adhesives. Starch is made up of highly branched chains of glucose units (10.6 A. per unit) (34). Sterling (34) reported that unmodified starch molecules are in the form of micelles which have a diameter of 90-110 A. The processing of coating grade starches is believed to disrupt the micelles and reduce the dimensions of the starch molecule (29). The calculated film thicknesses shown in Table V appear very reasonable as dimensions for the thickness of adsorbed adhesive films on the clay particles. The average adsorbed starch film appears to be about 5 glucose units thick.

Based on a starch density of 1.49 g./cc. and the average particle dimension given in Table I, a uniform and continuous starch film 47 A. thick would occur at a $f_p = 0.89$ for Type 2X clay and 0.94 for Burke's clay. The maximum in film volume occurred at starch levels which were lower than that required for complete coverage of pigment surface. It would be expected that the maximum separation in platelets would occur before each pigment surface is completely covered. Also electron micrographs showed the surface of the adhesive-covered particles to be rough and uneven. Therefore, the assumption of a uniform and continuous surface for this calculation is doubtful.

PVA is a linear polymer. This type of polymer has been shown to attach to the substrate surface and loop from the surface between points of attachment (30). This would allow for a buildup of an adhesive film thickness greater than the dimensions of the individual chain. A continuous and uniform PVA film 39 A. thick would occur at a $\frac{f}{p} = 0.92$ for Type 2X clay. Again, the maximum in the coating volume occurred before this level of adhesive was reached.

In order to test the encapsulation mechanism further, a third clay sample, Nu clay, was obtained which had a larger particle size. Nu clay was fractionated to remove the smaller particles and hereafter is called fractionated Nu clay. The thickness of the fractionated Nu clay was approximately 10 times as great as that of Type 2X clay. If the same thickness of starch layer found in Type 2X clay was adsorbed on the fractionated Nu clay, it was expected that the increase in film volume would be about 10% of that observed for Type 2X clay. Indeed, only a small increase in film volume from 0.854 cc./g. clay for the pigment film containing no adhesive, to 0.865 cc./g. clay for the starch coating in the region of adhesive concentration represents constant film volume. The values for the film volumes of the fractionated Nu clay-starch coatings are listed in Appendix IV, Table XII. The starch level at which the Nu clay coating films attained the maximum in film volume was not determined. Therefore, no attempt was made to measure the change in pore size from the porosimeter data.

The small change in film volume for the Nu clay-starch coatings is in agreement with and further supports the suggested mechanism of particle encapsulation. The percentage increase in the overall film volume due to the adsorbed layer of adhesive, decreases with increasing particle thickness.

It was concluded from the foregoing results that encapsulation of the pigment particles was responsible for expansion of the coating structures when initial

increments of adhesive were added to the coating systems. It was demonstrated that the pigment particles were encapsulated by a layer of adhesive, the thickness of which was independent of the size of the clay particles. No continual buildup of the adhesive layer was found. The maximum thickness of adhesive layer was approximately 47 A. for starch and 39 A. for PVA. These values of adhesive film thickness were reasonable when compared to the size of the polymer molecules. In addition, it was shown that it was valid to use Equation (4) in conjunction with porosimeter data to calculate the dimensions of the slot-type pores found in coating structures.

MECHANISM BY WHICH THE ADHESIVE-PIGMENT INTERACTION
AFFECTS THE STRUCTURE OF COATING FILMS

The results in the preceding sections have shown that there was an interaction between the adhesive and clay pigment which influenced the structural formation of the coatings. The structures of the coatings were shown to undergo three distinct changes as the amount of adhesive was increased. The mechanism of how the interaction between the adhesive and pigment caused the changes in film structure was determined.

The initial change in film structure, as the first increments of adhesive were added, was an increase in film volume and average pore size. The adhesive material adsorbed on the surface of the pigment particles, thus increasing their effective particle size. These encapsulated particles packed in a manner which increased the pore size and film volume. The thickness of the adsorbed layer of adhesive was the same for pigment particles of different sizes. Coating films made from the smaller clay particles exhibited the largest increase in film volume.

The initial increase in coating film volume was followed by a range of adhesive concentrations in which the film structure remained constant. There appeared to be no further buildup of the binder on the clay particles, once the pigment particles were initially encapsulated with adhesive. Instead the added increments of adhesive were free to migrate and fill the smaller pores as the coatings dried. The range of adhesive concentrations over which the film volume remained constant depended upon the type of adhesives used in preparing the coatings.

The third change in the structure of the pigment films was a compaction in which the film volume decreased and the pore size distribution became narrower until all of the pores were filled with adhesive. The adhesive level at which the compaction was first initiated depended upon the type of binder used in preparing the

coatings. The compaction of the coating film was believed to be the result of the formation of a "continuum or gel" structure of adhesive material which completely encompassed the pigment particles during drying. This "gel" surrounded the pigment particles before they had a chance to form the normal pigment skeleton and drew the particles together in a more compact state as the "gel" dried.

The physical property of the adhesive which appeared to determine the concentration at which the "gel" formed was the degree of hydration of the polymer. Polyvinyl alcohol has a high degree of hydration which was manifested in the rapid increase in viscosity at low solids content. The PVA films started to compact at a $\bar{f}_p = 0.92$ as compared to $\bar{f}_p = 0.82$ for the starch.

The viscosities of the starch solutions did not increase until a higher solids content was reached. The viscosities of the dextrinized and oxidized starches were quite similar over the same range of temperatures and solids content. The concentration of adhesive at which the coatings film started to compact was the same for both starches.

Further evidence supporting the view that a "gel" structure formed during drying and caused the coating film compaction, was the change observed by Burke (2) in the structure of clay-latex coatings. Because of the nature of emulsion latex particles, it would not be expected that such a "gel" could form. Therefore, this type of film compaction would not be expected to occur in latex coatings and Burke found that it did not.

The structure of the clay coatings were found to undergo an initial increase in film volume and pore size due to the encapsulation of the pigment particles by a layer of adhesive. After the initial increase, the structure of the coating films remained constant with the added increments of adhesive filling the smaller

pores. As the adhesive concentration was further increased, a level was reached at which a "gel" was formed that caused the film structure to compact.

The adhesive level at which the "gel" was formed, corresponds closely to the concentrations at which PVA and starch are used in the coating industry (1). It is possible that there is a significant change in film strength occurring at the adhesive "gel" concentration.

SUMMARY AND CONCLUSION

SUMMARY OF EXPERIMENTAL WORK

It was confirmed that the adhesive has a significant role in determining the structure of pigment coatings. The structure of starch and polyvinyl alcohol coatings were found to undergo three distinct changes as the adhesive level was increased. The film volume and pore size of the coatings were found to increase as the first increments of adhesives were added. Once the adhesive level was raised to 2.5 parts PVA or 4.0 parts starch per 100 parts clay, the film volume remained constant. The additional adhesive was found to migrate and fill the smaller pores. The final change in structure was a compaction of the pigment skeleton which occurred at 8 parts PVA or 22 parts starch per 100 parts clay. The film volume decreased and the pore size distribution became narrower until all of the pores were filled with adhesive.

Several possible mechanisms including flocculation, changes in surface tension, and adhesive encapsulation of the pigment particles were proposed and tested to explain the observed changes in coating film structure.

Flocculation could have been occurring by polymeric bridging of the pigment particles, or by "robbing" of the dispersing agent from the pigment particles. The flocculation studies carried out, including filtration rate, viscosity, and direct particle size measurements, showed that neither type of flocculation was occurring in the coating colors being investigated in this work. However, the filtration rate studies of the Cato 8 starch-clay system showed that the polymeric bridging type of flocculation could be detected in a kaolin clay system if the right polymer was selected.

The presence of starch and PVA were found to lower the surface tension of the coating colors. However, it was shown that it was possible to reduce the surface tension below the levels reached in the coating colors and not change the packing characteristics of the clay pigment particles.

In the evaluation of the possible encapsulation mechanism, it was necessary to develop techniques to measure the thickness of the adsorbed adhesive layer. It was shown that the data obtained from the mercury intrusion of the pigment skeleton can be used to determine the dimensions of the slot pores which exist in a coating. The measurement of the changes in slot diameter and the overall film volume have shown the average adsorbed layer of PVA to be 39 A. and starch to be 47 A.

CONCLUSIONS

The following conclusions are based on the results of this study of the structure of clay coatings.

The majority of the pores in a clay coating are of the slot form, the width of which is determined by the thickness of the clay platelets. Upon the addition of an adhesive to a clay slurry, there is an interaction between the binder and pigment which plays a significant role in determining the structure of the resulting clay coatings. This interaction was shown not to be the result of a flocculation or surface tension mechanism.

The initial increase in film volume and pore size as the first increments of adhesive are added is explained by the adsorption of the adhesive on the surface of the pigment which would increase the effective particle size. These larger encapsulated particles pack in a less dense manner because of the layer of adhesive

separating the clay platelets. The thickness of the adsorbed layer is independent of the size of the clay particles.

Once the particles are encapsulated with adhesive, there is no further buildup of the binder or further increase in film volume and pore size. Any additional adhesive migrates within the pigment skeleton and fills the smaller pores.

An adhesive level is reached for PVA and starch adhesives at which a "continuum or gel" is formed which encompasses the pigment particles before the final structure is set. As this "gel" dries, the pigment film undergoes a compaction in which the film volume decreases and the pore size distribution becomes narrower until all the pores are filled.

SUGGESTIONS FOR FUTURE WORK

The following suggestions for possible future investigations related to the structure of pigment coatings have evolved during the course of this study:

1. A study of the influences of substrate porosity upon the effect of adhesives on film structural development is needed. It is expected that the same structural changes observed in current study would also occur in coating films formed on a porous substrate.
2. A study should be made to determine how the end-use properties such as gloss, opacity, ink receptivity, and adhesive demand are related to the structure of coatings.
3. The influence of drying rate should have a marked effect on the formation of coating structure and thus is an area which warrants further work.

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APPENDIX I

DATA ON CLAY PARTICLE SIZE MEASUREMENTS

TABLE VI

SIZE OF TYPE 2X CLAY PARTICLES

Set No.	Length		Thickness	
	Average Set Length, μm .	Percent by Number	Average Set Thickness, μm .	Percent by Number
1	0.06	11.7	0.01	32.5
2	0.19	28.5	0.03	32.1
3	0.31	20.6	0.05	15.9
4	0.44	14.1	0.07	8.8
5	0.56	9.6	0.09	3.9
6	0.69	3.8	0.11	1.6
7	0.81	3.9	0.13	2.3
8	0.94	3.3	0.15	0.6
9	1.06	2.6	0.17	0.6
10	1.19	1.2	0.19	0.6
11	1.31	1.0	0.21	0.6
12	1.45	0.7	0.23	0.3

TABLE VII

SIZE OF BURKE'S CLAY PARTICLES

Set No.	Length		Thickness	
	Average Set Length, μm .	Percent by Number	Average Set Thickness, μm .	Percent by Number
1	0.19	18.3	0.02	13.1
2	0.46	25.2	0.04	20.0
3	0.75	16.1	0.06	20.3
4	1.02	10.9	0.09	12.1
5	1.29	8.4	0.11	12.8
6	1.57	8.1	0.13	7.2
7	1.75	4.0	0.15	6.9
8	2.02	4.7	0.17	3.1
9	2.30	1.2	0.19	2.8
10	2.57	1.6	0.21	0.7
11	2.85	0.6	0.24	0.0
12	2.12	0.9	0.26	1.0

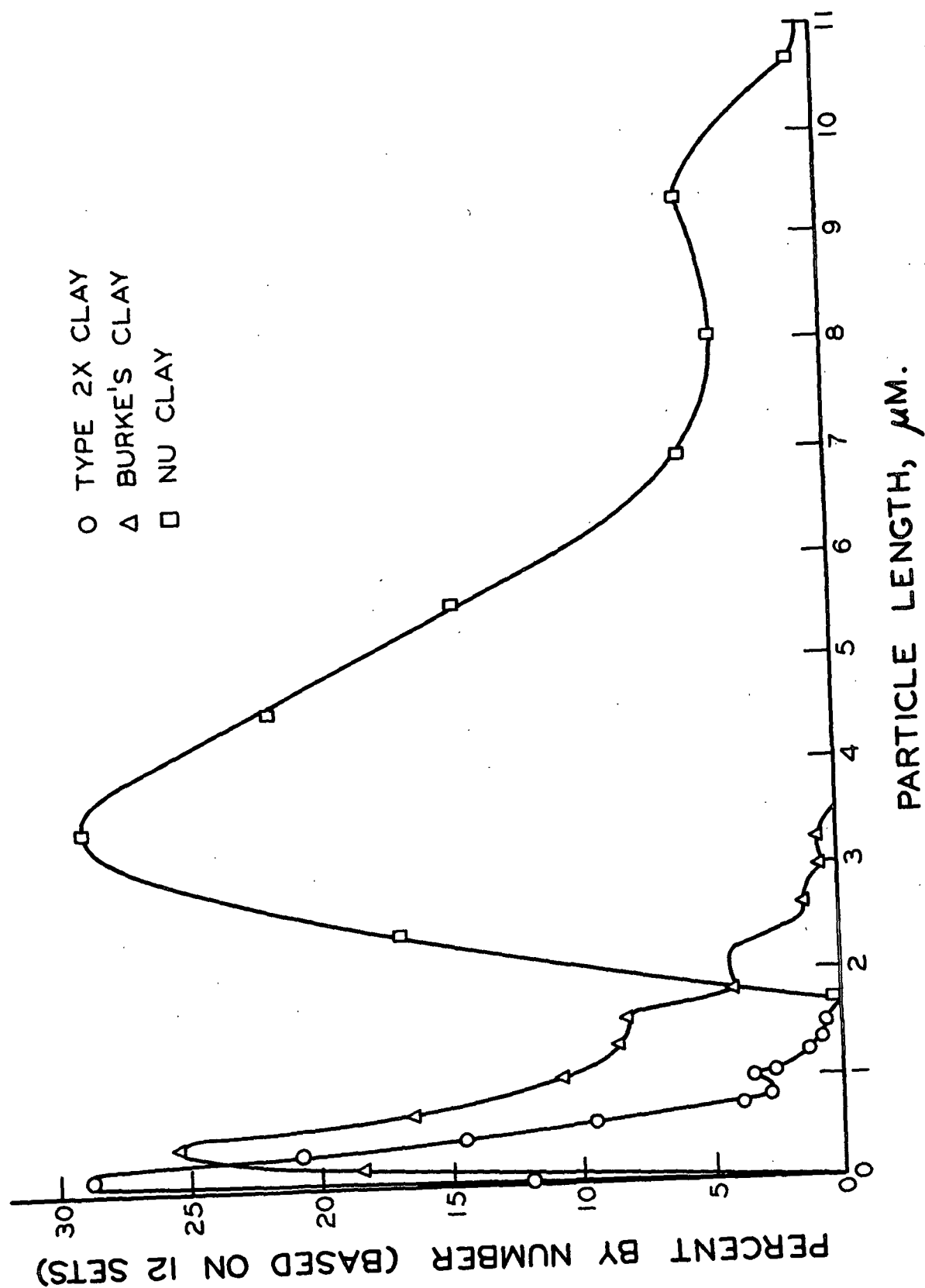


Figure 24. Distribution of the Particle Lengths of Type 2X, Nu, and Burke's Clay

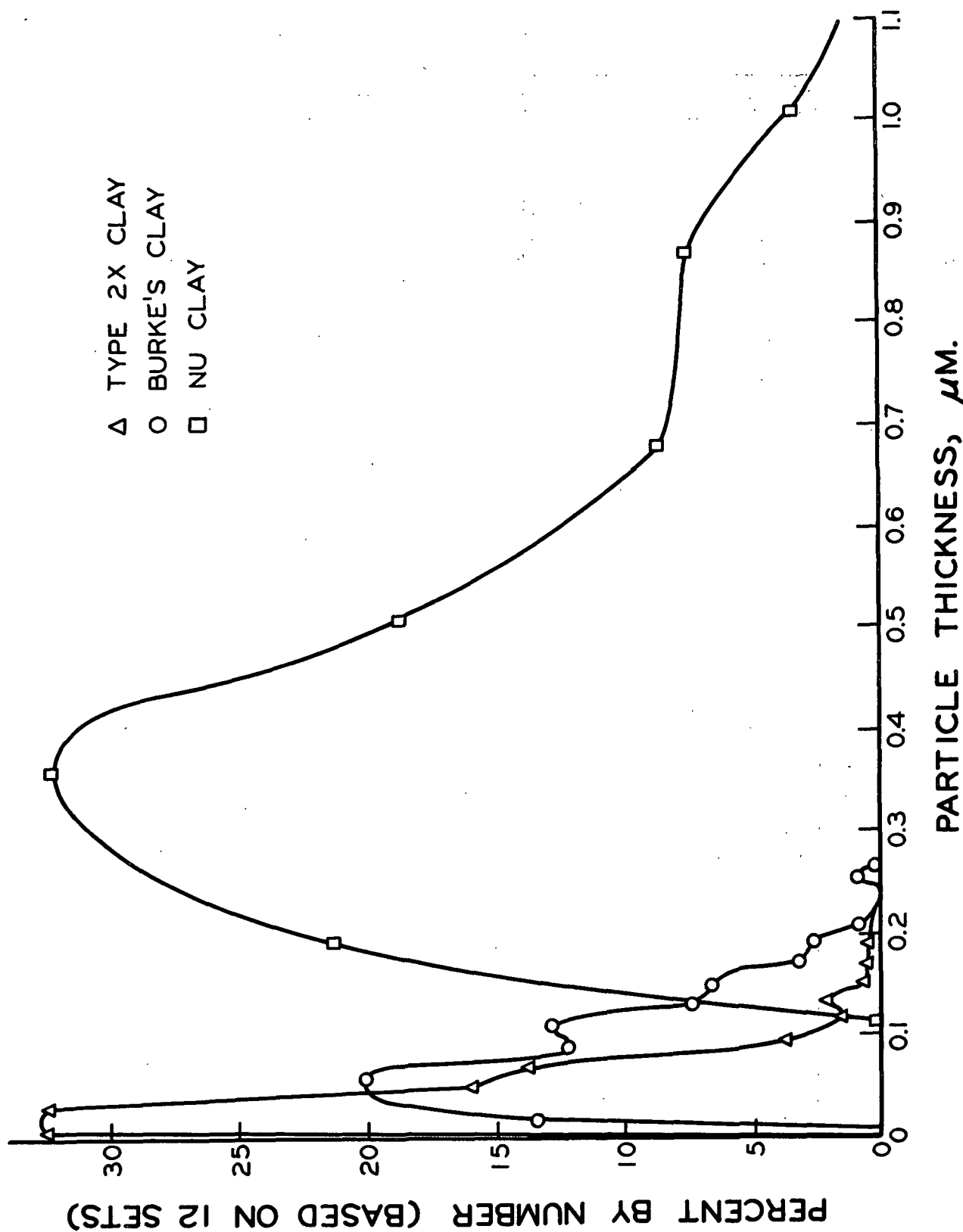


Figure 25. Distribution of the Particle Thicknesses of Type 2X, Nu, and Burke's Clay

TABLE VIII

SIZE OF NU CLAY PARTICLES

Set No.	Length		Thickness	
	Average Set Length, $\mu\text{m.}$	Percent by Number	Average Set Thickness, $\mu\text{m.}$	Percent by Number
1	2.4	16.1	0.19	21.1
2	3.5	28.6	0.36	34.4
3	4.6	21.4	0.51	18.9
4	5.6	14.3	0.68	8.9
5	6.9	5.4	0.87	7.8
6	8.1	4.5	1.02	3.3
7	9.5	5.4	1.11	1.1
8	10.6	0.9	1.34	3.3
9	11.8	0.0	1.51	0.0
10	12.5	0.9	1.68	0.0
11	14.0	1.8	1.84	0.0
12	15.9	0.9	2.09	1.1

APPENDIX II.

COMPARISON OF EXPERIMENTAL TECHNIQUES FOR
MEASURING SPECIFIC VOLUMES OF COATINGS

TABLE IX

COMPARISON OF TECHNIQUES FOR MEASURING
SPECIFIC VOLUMES OF COATINGS

Coating Sample		Specific Volume Determined by Porosimeter, cc./g.	Specific Volume by Measuring Physical Dimensions, cc./g.
Type			
2X Clay	$\frac{f}{p}$		
PVA	0.804	0.504	0.505
PVA	0.810	0.515	0.514
PVA	0.819	0.535	0.518
PVA	0.871	0.576	0.618
PVA	0.905	0.639	0.621
Starch	0.896	0.670	0.662
Starch	0.947	0.676	0.693
Starch	0.960	0.705	0.735
Burke's			
Clay	$\frac{f}{p}$		
Starch	0.776	0.607	0.606
Starch	0.845	0.738	0.706
Starch	0.892	0.711	0.706
Starch	0.906	0.752	0.735

APPENDIX III

DESCRIPTION OF THE EXPERIMENTAL PROCEDURES AND TECHNIQUES USED IN FLOCCULATION STUDIES

FILTRATION RATE STUDIES OF COATING COLORS

The objective of the filtration experiments was to determine the concentration of adhesive which would cause the maximum pigment flocculation. This concentration is found by measuring the filtration rate as a function of adhesive content. Such a determination is shown diagrammatically in Fig. 26.

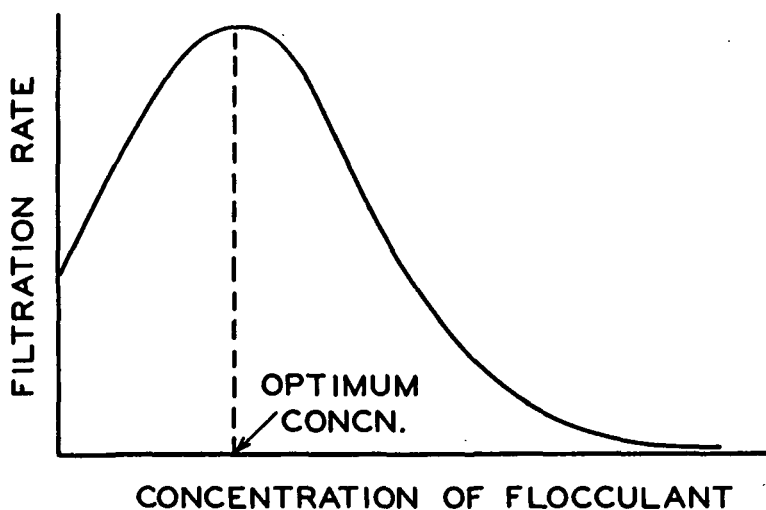


Figure 26. Filtration Rate vs. Concentration of Flocculant at Constant Pigment Content

The filtration rates measured are actually refiltration rates made by passing filtrate back through the formed bed and determining the time required to collect a given volume. The apparatus used to make the filtration measurements is shown in Fig. 27. A Millipore filter device was chosen because of its constant cross-sectional area and the ease of using pressure as well as vacuum in controlling the pressure drop across the filter. It was found that the adhesives used in coatings plugged the pores of the various Millipore filters tried, and therefore, Whatman No. 42 filter paper was chosen for the filtration experiments.

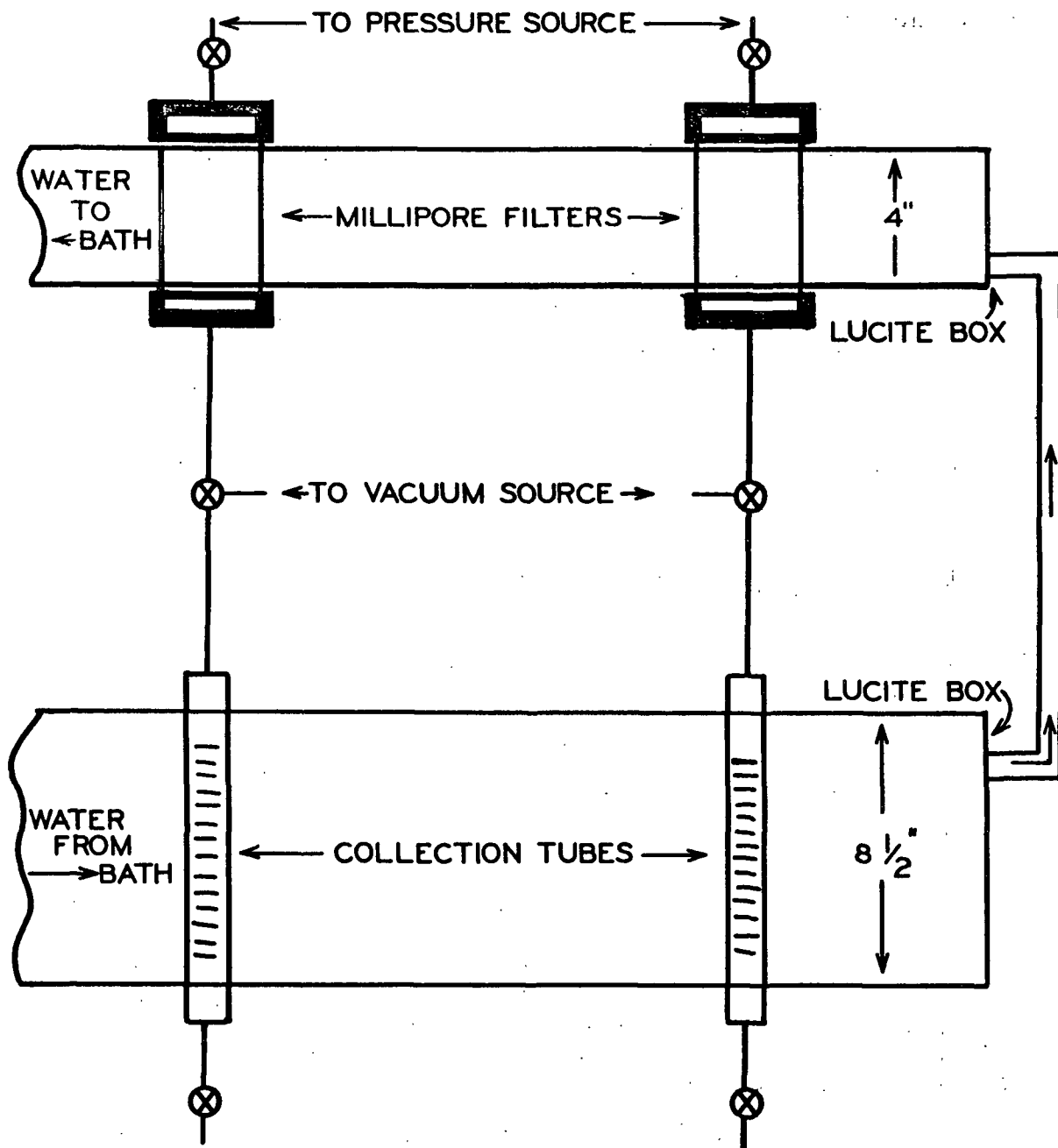


Figure 27. Millipore Filter Apparatus for Filtration Studies

The Millipore filter and collection tube were encased in a Lucite plastic box through which water passed from a constant temperature bath. This reduced the chances of error from changes in viscosity of the liquid due to changes in temperature.

Clay used in the filtration studies was dispersed at 70% solids in the same manner as when preparing coating colors. The adhesives were also prepared in the same manner as for coating colors. La Mer (14) indicated that the length of mixing time, intensity of mixing, and sequence of additions of reagents strongly influenced the flocculation process. These variables were investigated and the following set of conditions was found to provide the optimum chance for flocculation to occur.

The filtration samples were made up at 2% solids (1 g. of clay and 49 g. water). The necessary amounts of water and adhesive were placed in a 100-ml. beaker and mixed together for 5 min. with a Lightnin' mixer using a propeller-type blade rotating at 60 r.p.m. The clay was added over a 10-sec. period and the mixing was continued for 3 min. The sample was poured into the Millipore filter chamber in which the filter paper had been prewet with distilled water. The pressure drop across the filter pad was established at 43 p.s.i. The filtrate was collected until the liquid level in the Millipore chamber reached the top of the filter cake. The filtrate was then carefully poured back into the Millipore chamber and the rate determined as the filtrate passed through the pad for the second time. The rate was generally constant as the entire amount of filtrate passed through the filter pad. The filtration rates were expressed in ml./(min.) (cross-sectional area of pad, cm.²) (g. of clay). The area of the filter was 13.9 cm.².

ADHESIVE DIFFUSION STUDY

A possible cause of the flocculation of coating colors, other than polymeric bridging, was suggested by McEwen (17). It was believed that starch could possibly "rob" the dispersing agent from clay thus causing the clay to flocculate. The role

of the dispersing agent in stabilizing a kaolinite suspension is discussed by Michaels (35). Viscosity of a well-dispersed 50% solids clay slip was measured as a function of time in contact with 5% solids solutions of PVA and dextrin starch. The adhesive and clay were separated by a membrane of viscose dialyzing tubing in a diffusion cell built by Holtzman (36) during his work studying the stability of kaolinite-water systems. No adjustment was made in the pH of the adhesives. The diffusion cells were agitated on a horizontal shaker during the course of the study.

The viscosity measurements were made with a low-shear capillary viscometer developed at The Institute of Paper Chemistry. This viscometer consisted of two 100-ml. graduates placed side by side with their bases cemented to a brass block. The graduates were connected by a horizontal stainless steel capillary tube passing through the glass walls at the 10-ml. level that had a radius of 0.0583 cm. and was 5.04 cm. long. The driving force is supplied by the differential head between the two sides of the capillary. The viscosity was measured by pouring 100 ml. of the clay slip into one of the graduates and determining the time for the level to rise from the 20-ml. to the 40-ml. level in the other graduate. The viscosity is expressed in seconds required to collect 20 ml.

McEwen (17) reported that both starch and PVA had the ability to imbibe water away from clay through a viscose membrane. Therefore, in the diffusion study it is necessary to correct any increase in viscosity for that portion caused by the imbibition of water. This is done by constructing a curve in which the viscosity is plotted versus percent solids clay. If the only affect of the adhesive in the diffusion study is to remove water, the viscosity will follow along the viscosity versus percent solids curve. However, if there is an interaction which causes flocculation, then the viscosity will be above this curve.

VISCOSITY MEASUREMENTS OF COATING COLORS

The low-shear capillary viscometer was used to measure the viscosity of a series of starch-clay coating colors. In this series of coating colors, the amount of starch was increased while holding the clay-to-water ratio equal to one. The purpose of this study was to determine if there was any abrupt change in the viscosity of the coating colors as a function of starch content, which could possibly be an indication of the onset of flocculation. The coating colors were prepared in the standard manner with the starch concentration covering the range in which the coating structures underwent expansion.

PARTICLE SIZE MEASUREMENTS OF COATING COLORS

The extent of flocculation could be measured by the change in the size of particles in the coating colors. The size of coating particles was measured before and after the addition of an adhesive. If flocculation did occur, it is expected that the particle size would increase. The techniques used to measure the particle sizes are discussed in the following sections.

COULTER COUNTER

The Coulter Counter (16) can be used to determine the number and size of particles suspended in an electrically conductive liquid. This is done by forcing the suspension to flow through a small aperture having an immersed electrode. As a particle passes through the aperture, it changes the resistance between the electrodes and produces a voltage pulse of short duration having a magnitude proportional to the particle size. The series of pulses is then electronically scaled and counted.

The electrically conductive liquid used in these studies was a 1% NaCl solution. Clay will flocculate by itself in a 1% NaCl solution. However, the dilute suspension

used and the short time required to obtain the measurement permits the determination of the particle size before flocculation has occurred to any great extent.

The coating colors were prepared in the standard manner and diluted to 0.1% solids. The size of the particles in the coating colors were compared to those in a clay slip which had been dispersed in the standard manner and also diluted to 0.1% solids. The 30 nm. aperture was used in the Coulter Counter.

OPTICAL MICROSCOPE

Individual clay particles are visible when viewed through an oil immersion lens of a Bausch and Lomb microscope at a magnification of 1000X. Coating colors were prepared from starch and PVA at an $f_p = 0.90$ in the normal manner, then diluted to 0.1% solids. In checking for flocculation, the size of normal clay particles were compared to those of a clay which had been made into coating colors. Pictures were taken at 1000X of the various clay samples after they had been placed in glycerin to slow down their Brownian motion.

SURFACE TENSION MEASUREMENTS

Surface tension measurements were made of the clay slurries, adhesives, and coating colors with a Du Nuoy Interfacial Tensiometer. The surface tension of the clay slurries and coating colors were measured at a clay-to-water ratio equal to one. All measurements were made at room temperature.

APPENDIX IV

SPECIFIC VOLUMES OF COATING FILMS DETERMINED BY POROSIMETER

TABLE X

SPECIFIC VOLUMES OF TYPE 2X CLAY -
DEXTRINIZED STARCH COATINGS

Pigment Weight Fraction, $\frac{f_p}{p}$	Film Specific Volume, cc./g.	Starch Volume, cc./g. clay	Film Volume, cc./g. clay
1.0000	0.6530	0.0000	0.6530
0.9877	0.6629	0.0084	0.6711
0.9797	0.6617	0.0140	0.6754
0.9675	0.6758	0.0227	0.6985
0.9598	0.7049	0.0282	0.7344
0.9465	0.6927	0.0410	0.7319
0.9258	0.6924	0.0540	0.7481
0.8964	0.6695	0.0783	0.7469
0.8749	0.6518	0.0970	0.7450
0.8407	0.6305	0.1275	0.7499
0.7940	0.5736	0.1753	0.7224
0.7661	0.5367	0.2121	0.7051
0.7382	0.5101	0.2396	0.6910
0.7119	0.4656	0.2735	0.6540
0.0000	0.6701 (A film of starch with no clay present)		

TABLE XI

SPECIFIC VOLUMES OF STARCH-CLAY
COATINGS PREPARED BY BURKE

Pigment Weight Fraction, $\frac{f_p}{p}$	Film Specific Volume, cc./g.	Starch Volume, cc./g. clay	Film Volume, cc./g. clay
1.0000	0.7507	0.0000	0.7505
0.9670	0.7843	0.0230	0.8111
0.9620	0.7787	0.0266	0.8095
0.9401	0.7638	0.0429	0.8125
0.9058	0.7422	0.0702	0.8194
0.8918	0.7113	0.0816	0.7976
0.8866	0.7250	0.0882	0.8177
0.8451	0.7023	0.1235	0.8310
0.8036	0.6559	0.1645	0.8162
0.7756	0.6072	0.1955	0.7829
0.7589	0.6169	0.2145	0.8129
0.7134	0.5136	0.2710	0.7199

TABLE XII

SPECIFIC VOLUMES OF TYPE 2X CLAY -
OXIDIZED STARCH COATINGS

Pigment Weight Fraction, $\frac{f_p}{P}$	Film Specific Volume, cc./g.	Starch Volume, cc./g. clay	Film Volume, cc./g. clay
1.000	0.6400	0.000	0.640
0.993	0.6785	0.005	0.683
0.987	0.6720	0.009	0.680
0.928	0.6746	0.055	0.727
0.922	0.6753	0.060	0.733
0.904	0.6610	0.075	0.731
0.884	0.6596	0.092	0.746
0.860	0.6481	0.116	0.753
0.831	0.6255	0.146	0.753
0.826	0.6187	0.149	0.744
0.803	0.5977	0.174	0.744
0.800	0.5818	0.177	0.727
0.746	0.5289	0.241	0.703
0.740	0.5133	0.249	0.694
0.730	0.4995	0.262	0.683
0.706	0.5063	0.295	0.719

TABLE XIII

SPECIFIC VOLUMES OF TYPE 2X CLAY -
POLYVINYL ALCOHOL COATINGS

Pigment Weight Fraction, $\frac{f_p}{P}$	Film Specific Volume, cc./g.	PVA Volume, cc./g. clay	Film Volume, cc./g. clay
1.0000	0.6530	0.0000	0.6530
0.9941	0.6950	0.0045	0.6991
0.9907	0.7071	0.0072	0.7137
0.9790	0.7109	0.0165	0.7261
0.9747	0.7000	0.0200	0.7182
0.9714	0.7019	0.0226	0.7226
0.9679	0.6999	0.0255	0.7231
0.9397	0.6880	0.0493	0.7321
0.9045	0.6386	0.0815	0.7060
0.8713	0.5760	0.1210	0.6611
0.8488	0.5351	0.1370	0.6304
0.8096	0.5142	0.1810	0.6351
0.8037	0.5037	0.1884	0.6267
0.7499	0.2572	0.2572	0.6397
0.0000	0.7693	(A film of PVA with no clay present)	

TABLE XIV

SPECIFIC VOLUMES OF NU CLAY -
DEXTRINIZED STARCH COATINGS

Pigment Weight Fraction, $\frac{f_p}{p}$	Film Specific Volume, cc./g.	Starch Volume, cc./g. clay	Film Volume, cc./g. clay
1.0000	0.8542	0.0000	0.8542
0.8552	0.7389	0.1129	0.8640
0.7511	0.8552	0.2209	0.8661

APPENDIX V

PORE SIZE FREQUENCY DATA FROM MERCURY POROSIMETER

TABLE XV

POSITION OF PEAKS ON POROSIMETER VOLUME FREQUENCY CURVES FOR TYPE 2X CLAY COATINGS

Starch Coatings		PVA Coatings	
Pigment Weight Fraction, $\frac{f}{p}$	Position of Peak, p.s.i.	Pigment Weight Fraction, $\frac{f}{p}$	Position of Peak, p.s.i.
1.0000	1,860	1.0000	1,860
0.9877	1,610	0.9941	1,710
0.9797	1,560	0.9907	1,560
0.9675	1,410	0.9790	1,460
0.9598	1,210	0.9747	1,410
0.9465	1,260	0.9714	1,410
0.9255	1,210	0.9679	1,410
0.8964	1,210	0.9397	1,460
0.8748	1,210	0.9045	1,860
0.8408	1,210	0.8713	2,610
0.7940	1,410	0.8488	None
0.7611	2,710	0.8096	None
0.7382	None		
0.7119	None		

TABLE XVI

POSITION OF PEAKS ON POROSIMETER VOLUME FREQUENCY CURVES FOR BURKE'S DEXTRINIZED STARCH - CLAY COATINGS

Starch Coatings		PVA Coatings	
Pigment Weight Fraction, $\frac{f}{p}$	Position of Peak, p.s.i.	Pigment Weight Fraction, $\frac{f}{p}$	Position of Peak, p.s.i.
1.0000	910	0.8866	710
0.9670	760	0.8451	705
0.9620	709	0.8036	710
0.9401	712	0.7756	820
0.9058	712	0.7589	810
0.8918	710	0.7134	None

APPENDIX VI

DATA ON FILTRATION RATE STUDIES

TABLE XVII

FILTRATION RATES OF TYPE 2X CLAY SUSPENSIONS

Weight, % polymer based on clay	Filtration Rates of PVA Suspensions, mil/min. cm. ² g. clay	Filtration Rates of Dextrin Starch Suspensions, mil/min. cm. ² g. clay
0.00	0.0768	0.0768
0.05	0.0745	--
0.10	0.0687	0.0750
0.50	0.0380	0.0586
1.00	0.0282	0.0631
2.50	0.0202	0.0450
6.00	0.0144	0.040
7.50	--	0.0200

TABLE XVIII

FILTRATION RATES OF BURKE'S CLAY SUSPENSIONS

Weight, % polymer based on clay	Filtration Rates of PVA Suspensions, mil/min. cm. ² g. clay	Filtration Rates of Dextrin Starch Suspensions, mil/min. cm. ² g. clay
0.00	0.273	0.273
0.05	0.267	--
0.10	0.195	0.273
0.50	0.124	0.260
1.00	0.115	0.224
5.00	0.061	0.085
10.00	--	0.014

TABLE XIX

FILTRATION RATES OF TYPE 2X CATO 8 STARCH SUSPENSIONS

Weight, % polymer based on clay	Filtration Rates, mil/min. cm. ² g. clay
0.0	0.074
0.5	0.111
1.0	0.130
2.5	0.153
3.0	0.194
3.5	0.438
4.0	0.426
4.5	0.258
5.0	0.138
10.0	0.042

APPENDIX VII

DATA ON LOW SHEAR VISCOSITY MEASUREMENTS
OF CLAY SUSPENSIONS

TABLE XX

VISCOSITY OF CLAY SLURRIES VS. PERCENT SOLIDS

Percent Solids of Clay Slurry	Time to Collect 20 mil, sec.
47.7	81
50.3	89
52.8	107
53.4	109
54.8	124
57.4	151

TABLE XXI

VISCOSITY DATA FOR DISPERSING AGENT DIFFUSION STUDY

Adhesive and Length of Contact Time	Time to Collect 20 mil, sec.	Percent Solids of Clay Slurry
Clay slurry at start	89	50.0
Starch - after 16 hr.	94	51.4
Starch - after 60 hr.	161	59.8
PVA - after 20 hr.	118	54.5

TABLE XXII

VISCOSITY OF TYPE 2X CLAY - DEXTRIN
STARCH COATING COLORS

Weight Percent Starch on Coating	Time to Collect 20 mil
0.00	90
0.55	101
1.10	115
1.65	135
2.20	158
2.75	176
3.30	200
4.40	263

APPENDIX VIII

PARTICLE SIZE MEASUREMENTS BY COULTER COUNTER

TABLE XXIII

PARTICLE SIZE OF TYPE 2X CLAY COATING COLORS

Particle Diameter (E.S.D.), μm .	Weight Percent Above a Stated Size		
	Type 2X Clay Slurry	PVA Coating Color	Starch Coating Color
5.37	0.4	0.5	0.2
4.26	0.6	1.5	0.8
3.38	1.3	3.4	1.8
2.68	2.8	5.3	3.5
2.13	5.4	9.1	6.2
1.69	11.3	16.8	16.4
1.34	25.3	31.6	23.1
1.07	54.9	59.2	61.2
0.85	100	100	100

APPENDIX IX

SURFACE TENSION MEASUREMENTS OF COATING COLORS

TABLE XXIV

SURFACE TENSION MEASUREMENTS OF TYPE 2X
CLAY COATING COLORS

Pigment Weight Fraction, $\frac{f_p}{p}$	Surface Tension of Coating Colors	
	Polyvinyl Alcohol, dynes/cm.	Dextrinized Starch, dynes/cm.
1.00	72.1	72.1
0.96	71.7	69.1
0.92	70.2	62.0
0.88	69.2	58.7
0.84	68.3	56.3
0.80	67.5	54.3
0.76	67.1	54.0

APPENDIX X

DETERMINATION OF WIDTH OF SLOT PORES IN CLAY COATINGS

TABLE XXV

SAMPLE CALCULATION OF WIDTH OF SLOT PORE FOR
TYPE 2X CLAY COATING

- Notes: 1. Coating contained no adhesive.
2. Slot width "d" calculated from Equation (4),
where $\underline{D} = 98.8/\underline{p}$.
3. Number of pores of a certain size equals total pore
volume/volume of one pore.

Pressure, p.s.i.	Slot Average		Volume of Mercury Intruded, cc./g. clay	Total Vol. of Pores, $\mu\text{m.}^3$	Volume of One Pore, $\mu\text{m.}^3$
	Width \underline{D} , $\mu\text{m.}$	Width, $\mu\text{m.}$			
1050	0.093		0.0000		
		0.091		17×10^8	0.02275
1160	0.089		0.0017		
		0.087		8	0.02175
1220	0.085		0.0025		
		0.083		8	0.02075
1280	0.081		0.0033		
		0.079		15	0.01975
1280	0.077		0.0048		
		0.075		10	0.01875
1330	0.073		0.0053		
		0.071		40	0.01775
1430	0.069		0.0093		
		0.067		11	0.01675
1520	0.065		0.0104		
		0.063		37	0.01575
1620	0.061		0.0141		
..
..
..
4700	0.021		0.2403		
		0.019		68	0.00475
5800	0.017		0.2471		
		0.015		22	0.00375
7600	0.013		0.2493		
		0.011		36	0.00275
11000	0.009		0.2529		

TABLE XXV (Continued)

SAMPLE CALCULATION OF WIDTH OF SLOT PORE FOR
TYPE 2X CLAY COATING

Slot Width " <u>D</u> ", μm .	Total No. of Pores (See Note 3)	Fraction of the Total Pores	No. of Pores, <u>D</u>
0.091	7.47×10^{10}	0.003	6.8×10^9
0.087	3.68	0.002	3.2
0.083	3.80	0.002	3.15
0.079	5.06	0.002	4.0
0.075	5.33	0.002	4.0
0.071	22.54	0.009	16.0
0.067	6.57	0.003	4.4
0.063	23.49	0.009	14.8
..
..
0.019	143.16	0.067	27.2
0.015	58.67	0.026	8.8
0.011	<u>130.91</u>	<u>0.057</u>	<u>14.4</u>
	2305.67×10^{10}	1.000	971.78×10^9

$$\text{No. Av. Slot Width} = \frac{\sum (\text{No. of Pores}) \frac{D}{\sum (\text{No. of Pores})}}{\sum (\text{No. of Pores})} = \frac{97.178}{2305.67} = 0.0422 \mu\text{m}.$$

TABLE XXVI

FREQUENCY OF SLOT WIDTHS FOR TYPE 2X CLAY COATINGS

Slot Width " <u>D</u> ", μm .	Fraction of Total Pores of the Stated Size		
	Clay Film No Adhesive	PVA Coating	Dextrinized Starch Coating
0.091	0.003	0.003	0.001
0.087	0.002	0.010	0.001
0.083	0.002	0.023	0.002
0.079	0.002	0.041	0.063
0.075	0.002	0.050	0.124
0.071	0.009	0.093	0.120
0.067	0.003	0.090	0.078
0.063	0.009	0.085	0.051
0.059	0.010	0.073	0.068
0.055	0.253	0.042	0.054
0.051	0.152	0.056	0.060
0.047	0.092	0.061	0.057
0.043	0.081	0.046	0.050
0.039	0.049	0.048	0.027
0.035	0.059	0.046	0.032
0.031	0.041	0.047	0.031
0.027	0.058	0.050	0.030
0.023	0.030	0.044	0.027
0.019	0.062	0.039	0.027
0.015	0.026	0.025	0.022
0.011	0.057	0.017	0.008

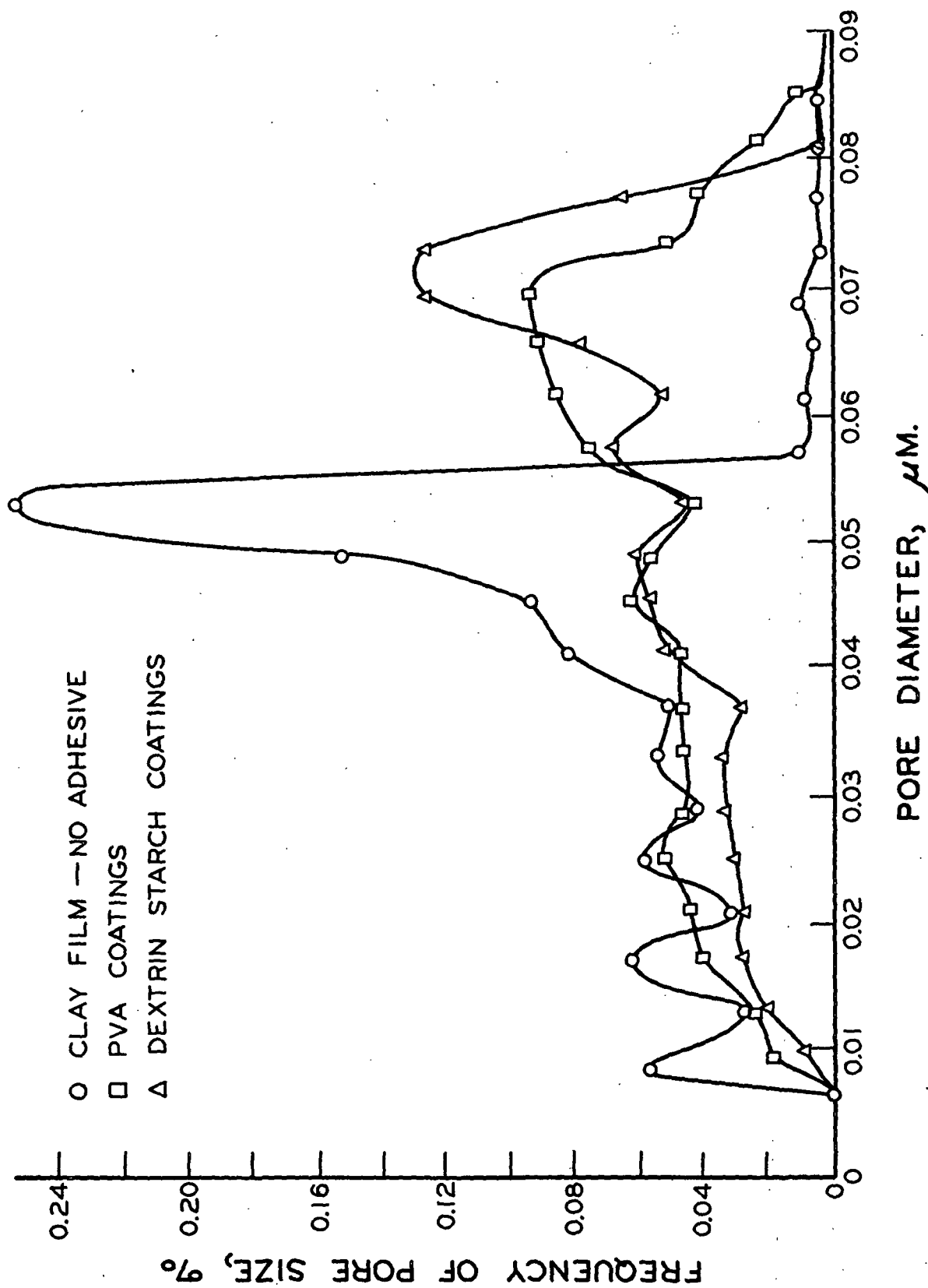


Figure 28. Frequency Distribution of Pore Diameters for Type 2X Clay Coatings

TABLE XXVII

FREQUENCY OF SLOT WIDTHS FOR BURKE'S COATINGS

Slot Width " <u>D</u> ", μm .	<u>Fraction of Pores of the Stated Size</u>	
	Clay Film No Adhesive	Dextrinized Starch Coating
0.158	0.003	0.015
0.150	0.003	0.034
0.142	0.004	0.065
0.134	0.004	0.103
0.126	0.006	0.063
0.118	0.026	0.046
0.110	0.167	0.050
0.102	0.132	0.067
0.094	0.079	0.052
0.086	0.057	0.057
0.078	0.066	0.027
0.070	0.061	0.046
0.062	0.040	0.036
0.054	0.083	0.065
0.046	0.036	0.062
0.038	0.040	0.051
0.030	0.066	0.060
0.022	0.065	0.05
0.014	0.057	0.015

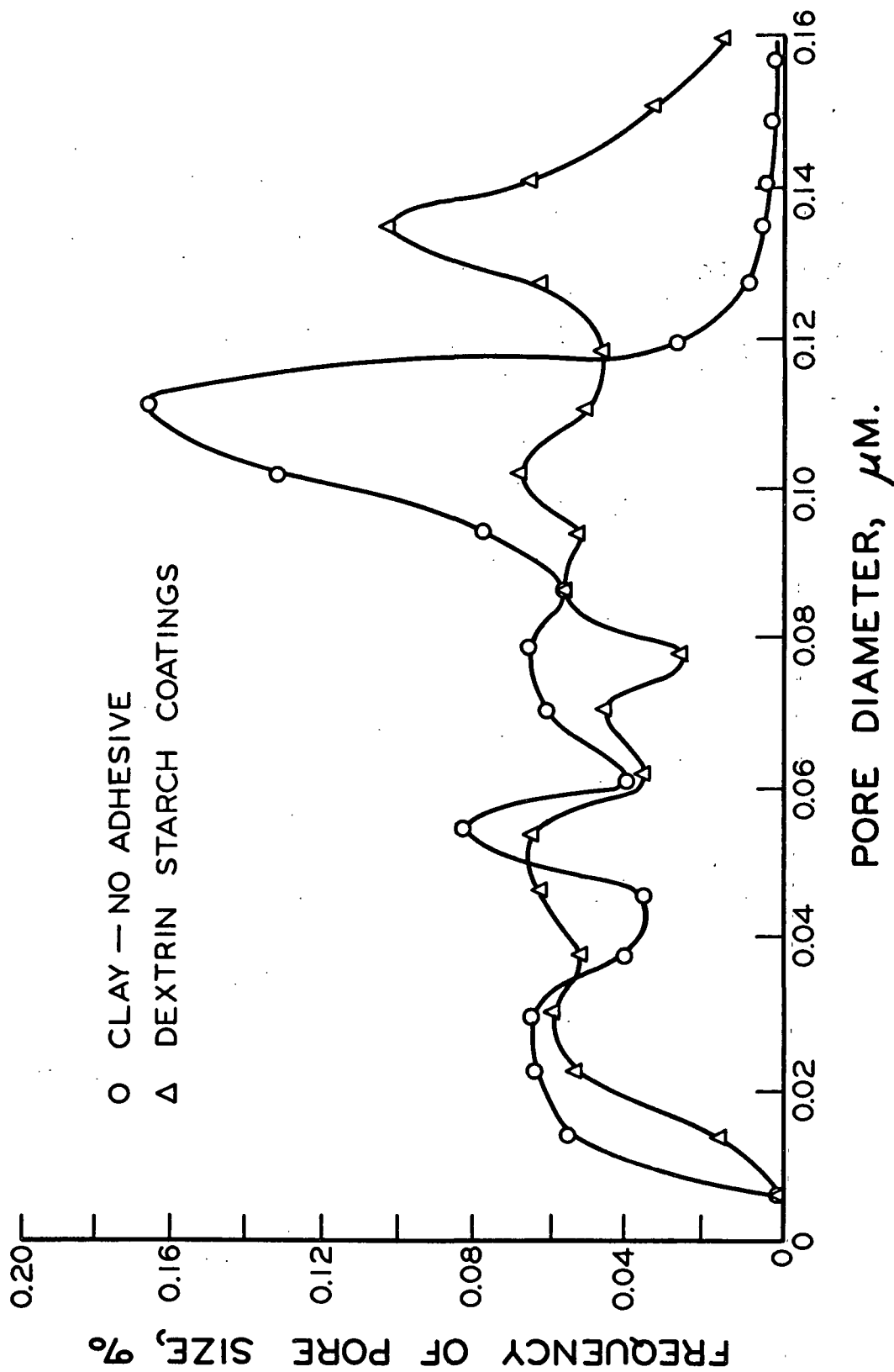
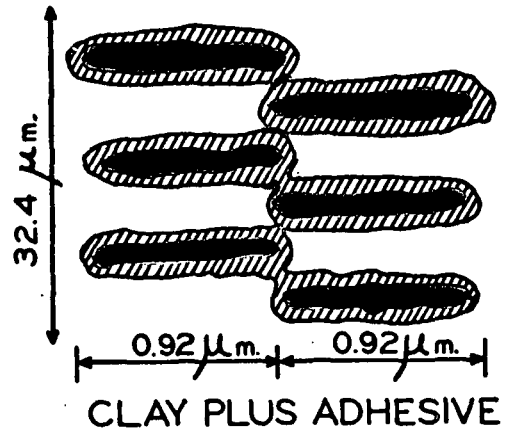
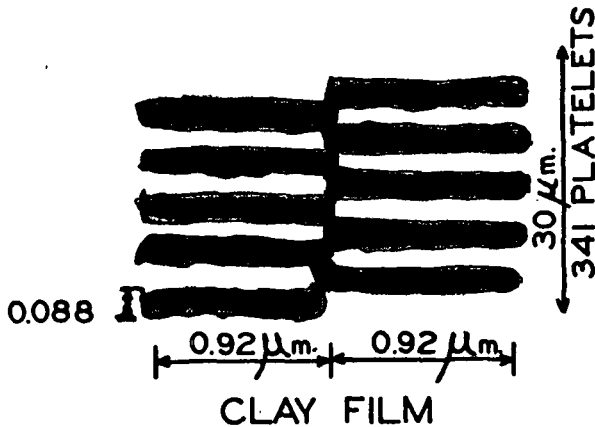


Figure 29. Frequency Distribution of Pore Diameters for Burke's Clay Coatings

APPENDIX XI

SAMPLE CALCULATION FOR DETERMINING THE THICKNESS OF THE
ADHESIVE LAYER FROM FILM VOLUME MEASUREMENTS

BURKE'S CLAY



- NOTES: 1. Clay platelets are assumed to be squares ($0.92 \times 0.92 \times 0.088 \mu\text{m}$.).
2. Typical coating is $30 \mu\text{m}$. thick.
3. Void volume for Burke's clay is 50%.

PHYSICAL PROPERTIES OF CLAY FILM

Volume of clay film = $50.8 \mu\text{m}^3$

Surface area = $688 \mu\text{m}^2$

Volume of pigment = $25.4 \mu\text{m}^3$

PHYSICAL PROPERTIES OF CLAY COATING

Data from film volume measurements.

1. Film volume no adhesive = $0.751 \text{ cc./g. clay}$

2. Film volume at maximum expansion
 $0.819 \text{ cc./g. clay}$

Ratio of expansion = $0.819/0.751$
This ratio is used to determine the
increase in coating pictured above.

Volume of coating = $55.5 \mu\text{m}^3$

Thickness increase = $2.4 \mu\text{m}$.

Thickness of adhesive layer =
 $2.4 \mu\text{m}/682 \text{ surfaces} = 35 \text{ A.}$