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SOME OBSERVATIONS ON DETERMINING THE SIZE OF PORES IN PAPER

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ABSTRACT

The various methods which have been used to determine the size of pores in paper are briefly reviewed. These are of three general types: (a) methods based on rate of efflux of fluids; (b) methods based on rate of rise of liquids in vertical strips; (c) methods based on the capillary pressure involved in penetration by liquids.

A new method is outlined, which takes advantage of the fact that the coefficient of slip of air in viscous flow through paper is a function of pressure. From the Meyer equation, the average effective pore radius is evaluated in terms of the air permeability values at two pressures. It is only necessary to determine the air permeability at two different pressures of an identical area of paper. Experimental values for two such air-permeability determinations on each of five papers, and the resulting values calculated for the average effective pore radius, are tabulated.

CONTENTS

I. METHODS AVAILABLE

1. INTRODUCTION

A number of attempts have been made to determine the size of the pores in paper. It may seem pointless even to broach the question of the size of the pores in such a structure, inasmuch as the free spaces in the network of fibers that constitute a sheet of paper are extremely irregular and indefinite in shape and size. The fact remains, however, that much effort has been expended in attempting to assign some numerical value to characterize the size of the pores in paper and various other materials. And the effort seems justified, both by the practical usefulness of such a numerical characterization and by the behavior of the materials. Although there is probably no such thing in a sheet of paper as a long, cylindrical capillary tube, the sheet, nevertheless, behaves in certain respects as if its system of pores were made up of a large bundle of such capillary tubes in parallel, making it possible to talk about and write equations for a system of pores that behaves in certain respects like the system of pores in an actual sheet of paper. It is very necessary, of course, that one keep in mind the limitations of such a contrivance. Let us suppose, for instance, that the channels are interconnected within the body of the sheet, as they possibly are in most papers. One might then, with good reason, look upon the whole network as a single pore, and pore size from such a viewpoint might not have any relation to pore size as defined from a different point of view.

2. TACIT DEFINITION

Most of the efforts that have been made to determine the size of pores in paper have concerned themselves with the behavior of fluids flowing within the structure of the sheet, and it is from this point of view that pore size has been tacitly defined by many workers. The values arrived at, of course, tell us little more than the average size, or the range of sizes, in a system of simple pores amenable to mathematical treatment which would behave, toward the flow of fluids, like the actual system of pores in the sheet. The sheet of paper does not necessarily contain any actual structural counterpart of the capillary system evaluated. The values for size of pores thus obtained have, nevertheless, been considered very useful in certain applications of paper and other porous materials. Some investigators have tried to interpret the results more nearly in accordance with reality by applying correction factors to accord with particular types of structure [3, 9,10].[1]

3. THE MICROSCOPE AS AN AID

The microscope is a valuable means of studying the pore structure of paper. It does not, however, give the same type of information as do flow measurements. It does not readily reveal which spaces are the pores or continuous channels, or how the spaces at different levels are connected. It is difficult to analyze the complex pattern that one sees in a magnified cross section of paper and to appraise it in terms of pores available for the transfer of fluids through the structure.[2] Although the dimensions seen with the microscope are highly significant as supplementary evidence, they cannot be regarded as having cardinal significance over values for pore size obtained through flow measurements. One cannot hope that they will do more than confirm the order of magnitude of values determined from actual flow measurements.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] A possible aid in this difficulty may be found in the suggestion of Dr. McPherson, of the Bureau staff, that a small amount of a gas, such as hydrogen selenide or hydrogen telluride, be mixed with the air that is being forced through the paper. Such a gas reacts with cellulose to dye it a distinctive color, which might aid one in tracing the air passages by sectioning the paper and examining it with a microscope.

4. METHODS BASED ON RATE OF EFFLUX OF FLUIDS

The estimation of pore size in paper through flow measurements has occupied the attention of several investigators during the past decade. Baird and Hrubesky [1] outlined methods of approach based on the work of Stamm [15] on wood sections. They proposed to make air-permeability measurements and apply the familiar Poiseuille equation, whereby the average effective radius, r (as defined by these workers), can be calculated from the permeability of the paper and the number and length of the capillaries in an equivalent system of parallel cylindrical capillaries. For necessary simplicity they assumed (as have other workers) the length of the air passages to be equal to the thickness of the paper.[3] Since the number of pores, N, is unknown, it was necessary to obtain, in addition to the Poiseuille equation, a second equation relating the average radius to the number of pores. Such an equation was formulated by determining the fractional pore area (equal to $\pi r^2 N$ per unit area of the sheet) as the ratio of the conductivity of a concentrated electrolyte saturating the paper to the conductivity of a free volume of the electrolyte equal to the volume of the paper.[4]

Although Baird and Hrubesky did not present definite values for pore size by their method, they gave values for pore space relative to the total air space, which indicate their belief that not more than 2 percent of the air spaces in a sheet of paper are continuous passages through the sheet available for the transfer of air. This would require the pores to be relatively large in order to account for the air permeability.

It may be of interest to note that Edwards [5], using the same general procedure on leather, estimated the average effective radius of the pores to be about 0.5 to 1 micron (thousandth of a millimeter) for the samples studied. He evaluated the fractional pore area by means of water-vapor–permeability data.

Manegold and Solf [9] made use of a somewhat similar procedure. They made permeability measurements with liquids and with air, expressing the results as specific permeability. They evaluated the fractional pore area as the ratio of the volume of liquid required to saturate a piece of paper, to the volume of the paper. Their values for the average effective pore radius of various papers ranged from 0.0007 to 8 microns, with values of a few tenths of a micron for most ordinary papers.

5. METHODS BASED ON RATE OF ASCENT OF LIQUID IN STRIPS

It has been shown that under certain conditions the radius of the bore in a glass capillary is proportional to the square of the height to which a liquid that wets it will rise in a given time [8, 19]. Simmonds [14], after presenting data to show that certain papers behave approximately in conformity with this relation when strips are hung with the lower end in water, applied this equation to evaluating the size

[3] The effective length of the pores through paper is almost certainly many times the thickness of the paper. In a previous publication [4] it was pointed out that the behavior of paper in air-permeability measurements demands a comparatively long path through the sheet. The fact that most fibers in paper are much flattened as a result of the pressure applied in calendering suggests that the channels between fibers may be likened to the spaces in a pile of overlapping flat plates. A fluid flowing down through such a structure would have to follow a very tortuous course back and forth between the surfaces of the plates, covering a distance many times the height of the pile. That part of the fluid traveling within the fibers of a sheet of paper would also follow a long path, since the fibers are nearly parallel to the plane of the paper.

[4] The electrolytic method of determining the fractional pore area was later repudiated by Stamm [16].

of the pores. He reported values for the average effective radius of the pores in cartridge paper board as about 0.008 to 0.045 micron; in blotting paper, about 0.1 to 0.3 micron; in sulfite pulp sheets, about 0.5 micron.

Foote [6] extended the experiments of Simmonds, using formamide, alcohol, and benzene, in addition to water. His experiments were made on sulfite bond, from a part of which the rosin sizing had been extracted so that readings could be obtained with water and formamide. His values for the average effective radius of the pores ranged from 0.006 to 0.35 micron, depending upon the liquid used in the experiments of capillary rise. He pointed out, however, that it may not be valid to assume that the contact angle is zero in all cases, and also that the equation used is probably not valid when the paper swells while the liquid is flowing through its structure. He considered his highest values (obtained with alcohol) to be the most credible.

Peek and McLean [13] measured the rate of rise of six organic liquids in strips of filter paper, and showed that the experimental data fitted their derived equation for the rate of rise. By evaluating the constants of their equation they were able, on the assumption of a uniform distribution of sizes, to calculate the range of pore sizes. They reported the values of 4 to 40 microns as the range of effective capillary radii of the filter paper with which they experimented. They included photomicrographs of cross sections of the filter paper to show that the widths of spaces presumed to be pores appear to lie within these limits.

6. METHODS BASED ON CAPILLARY PRESSURE

Larocque [7] forced oil at different pressures through paper and measured the time of transudation in each case. He then evaluated the capillary pressure by extrapolating the plot of pressure against the reciprocal of time to the zero value of the reciprocal of time to obtain a value for the pressure necessary to prevent penetration (pressure at infinite time of transudation). He then calculated the average effective capillary radius from the familiar equation of elementary physics, whereby the radius is twice the ratio of the surface tension of the liquid to the capillary pressure, for a liquid that wets the capillary. The value reported for the average effective pore radius in a supercalendered book paper was about 5 microns; in a bond paper, about 10 microns.

A modification of this procedure, involving the air pressure necessary to expel a liquid saturating a sheet of paper, was suggested by Baird and Hrubesky [1] as a means of evaluating the maximum pore radius of paper.

7. OTHER DATA AND METHODS

Witzmann [20] determined the average effective pore radius in filter paper and other filtering media, using several of the methods which have been outlined. He reported values for filter paper ranging from 0.05 to about 6 microns, depending on the method used and on the grade of filter paper tested.

Similar methods have been applied to the determination of pore size in other materials [2, 15, 17], and also an additional one involving the Kelvin relation of the curvature of a liquid in a capillary (and hence the radius of the capillary, when small) to the vapor pressure over the curved surface. This method, however, does not appear to have been adapted to the estimation of pore size in paper.

It is apparent from the foregoing review that it has been necessary to make liberal use of simplifying assumptions in evaluating pore size in paper, and that there is still some uncertainty about the order of magnitude of the size of the pores in this material.

II. A NEW METHOD

1. ORIGIN OF THE METHOD

In 1934 the writer found a more direct method of estimating the average effective pore size in a porous material, which does not appear to have been used before, and in view of the interest which has been manifested in the subject since that time, it seems desirable to describe it.

Bureau Research Paper RP682 [4] reported data showing that, by various criteria, the passages in a sheet of paper, through which air flows under a pressure difference across the sheet, behave as if they were a bundle of long capillary tubes in parallel. However, the effect of atmospheric pressure, or total pressure on air permeability did not seem to fit this interpretation. In this work Meyer's [11] equation for the efflux of a gas from a capillary tube was used, with the customary omission of the term containing the slip coefficient, inasmuch as for most situations it is valid to assume that the movement of the layer of fluid in contact with the walls of the capillary is so small as to be negligible. A short time after the paper was published, Guy Barr, of the National Physical Laboratory in England, pointed out that, whereas the omission of the term containing the slip coefficient would make no perceptible difference in evaluating the effect produced by other variables studied, it might make a difference in the case of a change in total pressure if the capillaries were small enough, inasmuch as the slip coefficient is a function of pressure. The data were reexamined in the light of Dr. Barr's suggestion, and it was found that a very probable value of the average effective pore radius could be obtained from the pressure-permeability data.

This interpretation of the total-pressure effect renders some of the conclusions in RP682 about this variable subject to revision, and brings into harmony all of the criteria used as evidence of the nature of the air passages in paper. It is not necessary to assume an elastic expansion of voids to explain the behavior, since the pressure criterion is no longer useful, inasmuch as an increase in air permeability with decreasing total pressure may be expected, regardless of the nature of the capillaries, when they are small enough.

2. SLIP COEFFICIENT

The Meyer equation for the viscous flow of a gas may be written

$$VP=\frac{\pi r^4 tD(2P-D)}{16L\eta}\left(1+\frac{4s}{r}\right), \tag{1}$$

in which V is the volume of gas, measured at the inlet pressure, P, which, in the steady state of efflux, enters the capillary in time, t, under a constant pressure difference, D, between the two ends; r is the radius of the capillary; L is its length; η is the coefficient of viscosity; and s is the coefficient of slip, which Meyer defines as the ratio of the coefficient of viscosity to the coefficient of friction on the walls of the capillary. Ordinarily the wall friction is so great that a layer of gas remains substantially fixed on the walls of the capillary, and the coefficient of slip becomes negligibly small in most applications of the equation. Actually, however, there is a slight movement, or slipping, of this surface layer in the direction of the gas stream, and it is this circumstance that affords the means to be described of estimating the size of the pores in paper. When r is small enough s/r cannot be neglected, and in paper we seem to have pores small enough to require that the slip factor be dealt with.

3. EQUATION FOR PORE RADIUS

The air permeability of paper is defined as the volume of air (measured at the inlet pressure) which flows through a unit area of the paper in unit time per unit pressure difference (the pressure difference used being always small in comparison with the total pressure). If, now, the average effective pore radius is defined as the radius of one of N identical cylindrical capillaries of length L in parallel, which, in combination, have the same air permeability as the paper under identical conditions, this air permeability, A, can be written

$$A=\frac{NV}{tD}=\frac{N\pi r^4}{8L\eta}\left(1-\frac{D}{2P}\right)\left(1+\frac{4s}{r}\right). \tag{2}$$

At some other inlet pressure, P', the air permeability, A', for a pressure difference, D' can be written in a similar manner. Dividing one equation by the other gives

$$\frac{A'}{A}=\frac{r+4s'}{r+4s}\cdot\frac{2PP'-PD'}{2PP'-P'D'} \tag{3}$$

since η is not a function of pressure. The last part of eq 3 will drop out, either when D and D' are so small in comparison with P and P' that the term is unity within experimental error (as was the case in the previous work) or when D and D' are chosen so that $PD'=P'D$.

The slip coefficient, s, is proportional to the mean free path of the molecules of the gas, and, in fact, is approximately equal to it [12]. That is, s is inversely proportional to the total pressure, or $sP=s'P'$. Therefore, from eq 3, with D and D' chosen as prescribed,

$$r=4s\frac{AP/P'-A'}{A'-A}. \tag{4}$$

If we take the slip coefficient equal to the mean free path, then s has a value of about 10^{-5} cm (0.1 micron), when P is 1 atmosphere. One has, therefore, only to make two determinations of the air permeability of a piece of paper at different total pressures, in order to calculate the average effective pore radius. Since from the form of eq 4, it is immaterial what unit is chosen for A and A', the air permeability will be reported in the customary unit.

4. EXPERIMENTAL VALUES

The apparatus used in determining the effect of change in total pressure, and described in RP682, was of the dual, differential-pressure type, with provision for changing the total pressure about 10 percent.

The calibration of the flowmeter would not be altered significantly by the change in total pressure in these experiments, because the radii of the glass capillaries used are large in comparison with the mean free path.

It may be well to emphasize that the experimental determination of the air permeability with this apparatus does not depend in any way upon the Meyer equation, and hence that a large ratio of slip coefficient to radius does not imply doubt about the accuracy of the determination. The equation was used in the previous work only as a means of interpreting the behavior of the paper. The values of A are subject to an uncertainty of probably less than 1 percent. The values of A', on the other hand, are probably somewhat more uncertain because of the increased difficulties of making the measurements, and because of possibly significant changes in testing conditions, such as in relative humidity resulting from the change in total pressure.

Table 1 gives the values obtained for the average effective pore radius calculated for 5 different papers by eq 4 from air-permeability measurements at two values of total pressure. These results are not inconsistent with evidence afforded by the microscope, and appear to be very probable values for the order of magnitude of the size of pores in paper. The values for the coated papers probably characterize the pore structure of the coating rather than of the paper that supports the coating. The relatively small air permeability of the bond paper, considering the size of its active pores, probably results from a marked decrease in the number of active pores, brought about by the plugging of most of the smaller passages with the glue sizing, which is normally concentrated near the surface in a bond paper.

TABLE 1.—*Average effective pore radius*

[Calculated from air-permeability measurements at two values of the total pressure, that is, for two values of the slip coefficient]

Paper	Air permeability in $\frac{\text{cm}^3/\text{sec}}{\text{m}^2\ (\text{g/cm}^2)}$		Average effective pore radius,
	A at 1 atm	A' at 0.9 atm	r
			Microns
Double-coated book paper	3.20	3.45	0.2
Single-coated book paper	6.95	7.40	.3
Ledger paper	37.5	39.0	.8
Machine-finished book paper	156.5	161.0	1.2
Bond paper	8.90	9.15	1.2

5. CONCLUDING REMARKS

It is not unlikely, as is suggested by the work of some of the investigators mentioned previously, that the effective size of the pores may be different for the three primary axes of paper. The results in table 1 are for flow normal to the plane of the sheet. It should not be difficult to devise an apparatus, making use of a mercury envelope, such as has been used by Stull and Johnson [18], with which air-permeability measurements at different pressures could be made in the lengthwise direction of strips of paper.

Although the method which has been outlined is applicable at ordinary pressures only to porous materials having a limited range of sizes of pores, it should be possible to extend the range by operating at low pressures, where the mean free path becomes correspondingly larger. The experimental difficulties would, of course, be increased, and a number of variables would come into more prominence.

With improvement in apparatus and technique, the slip-coefficient method of estimating pore size should be not without promise among the several less direct methods of approach which are available to investigators interested in learning more about the structural characteristics of paper and other porous materials.

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