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The Effect of Substrate Porosity and Method of Drying on Coating Gloss

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THE EFFECT OF SUBSTRATE POROSITY AND METHOD OF DRYING ON COATING GLOSS

by
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ABSTRACT

This thesis involved the study of the effects on gloss, smoothness, sizing, and ink holdout of average pore size and drying method for styrene butadiene, polyvinyl acetate, and acrylic bound pigmented coatings. Average pore size was varied by using four different substrates. A mylar film with 0 micron average pore size and Millipore filter papers with .22, .45, and .80 micron average pore size were used. The three drying methods used were back drying on a hot plate, air drying, and blow drying with hot air.

It was found that the styrene butadiene coating gave the best gloss development, the smoothest sheet, the best sizing, but the worst ink holdout. The polyvinyl acetate coating gave the second best gloss, smoothness, and sizing but the best ink holdout. The acrylic binder coating gave the least gloss development, smoothness, sizing, and ink holdout. The uncalendered gloss increased linearly from 3-4% between .22 and .80 microns average pore size. The gloss of the calendered sheets increased from .22 to .45 microns then decreased similarly from .45 to .80 microns. Blow drying gave the highest gloss followed by air drying then back drying. The smoothness was

unaffected by changing pore size for the uncalendered sheets. The Parker Print Surf smoothness tester results showed that smoothness increased as average pore size increased and smoothness increased after calendering. The Sheffield smoothness tester gave quite different results. The Sheffield smoothness decreased as average pore size increased and decreased after calendering. Back drying gave the smoothest sheet followed by air drying and blow drying. The only conclusions that can be drawn about sizing are that it decreased after calendering and polyvinyl acetate gave the best sizing followed by acrylic latex then styrene butadiene.. The ink holdout slightly decreased until about .45 micron average pore size then increased at a similar rate back to the initial value. Back drying gave the best ink holdout and blow drying gave the worst. Polyvinyl acetate gave the best holdout and styrene butadiene gave the worst.

INTRODUCTION

The purpose of this paper is to give a better understanding of the factors which affect the gloss of synthetic binder coatings. The literature survey is an indepth look at the factors affecting the development of the gloss of coated papers and surface properties associated with gloss development. The contents have been separated into five sections: the pigment portion of the coating, the binder portion, application variables, surface properties, and finishing conditions.

Following the literature survey is a description and discussion of an experiment to study the effects of changing substrate porosity on the gloss of styrene butadiene, polyvinyl acetate, and acrylic latex bound coatings. The effects of different drying methods on coating gloss was also investigated.

PIGMENT PORTION

Pigment Type

The affect of pigment type and shape on the gloss development of a coating has been studied by many different methods each designed to study a different aspect of pigment type. Gloss development of a 100% pigment is easiest for titanium dioxide which has small spherical-shaped particles. Gates, Windle, and Hines(1) determined that Satin White gives gloss much higher than most clays and is needle-like in shape. Kaliski(2) did extensive work with clays and he determined that after supercalendering, machine delaminated clay gives the highest gloss followed closely by #1 clay and then #2 clay. The delaminated clay is plate-like in structure and its superior gloss development is attributed to orientation of these plates. Calcium carbonate gives gloss less than many clays and is cigar-shaped.

Trader(3) showed that gloss increases fairly linearly with decreasing particle size and Lee(4) found that gloss can be improved by increasing the fraction of small particles. Kaliski(5) obtained higher gloss with a higher proportion of fines as long as the particles were the same shape. He theorized that the effect of the plate-like shape of delaminated clay is more significant than the effect of fines content. This is why delaminated clay gives higher gloss than #2 clay even though #2 clay has more fines. He said, "The

role of fines may be viewed as effective inhibitors of convection currents before the coating is solid and dissipators of stress afterwards."

Particle orientation has long been accepted as the means of gloss development in the supercalender, but this has been questioned and some new light has been shed on the role of particle orientation in paper gloss. Lapoutre(6) and Gates, Windle and Hines(1) found little or no correlation between particle orientation and gloss development in the supercalender. Gates found a high degree of orientation with Kaolin crystals but little correlation to gloss. It could be that the gloss of the uncalendered coating is affected by the degree of particle orientation, but gloss development in the supercalender is not due to further oreintation of the particles. Kaliski(2) found that the delaminated clay's shape makes it less sensitive to the roughness of the substrate than a #1 clay.

BINDER PORTION

Binder Type

It is well known that an all synthetic binder will lead to higher gloss than an all-natural binder. Regardless of coat weight or binder concentration, starch adhesives give a gloss 5-11 points higher than protein(7). Of the synthetic binders, Lapoutre(6) showed that styrene-butadiene latexes give slightly higher gloss than acrylics or vinyl acetate.

Acrylic and vinyl acetate binders give the same gloss at less than 20% higher. Polyvinyl acetate gave gloss about eight points higher than starch when 10% polyvinyl acetate and 8% starch coatings were compared(8). Walsh(7) studied combinations of synthetic and natural binders and found that an 80:20 latex to starch ratio gives the highest gloss, but for protein a 90:10 ratio gives highest gloss. He also compared synthetic binders for use on a gloss calender at 300^{o}F. At this high temperature, all latexes were found to give the same gloss. He suggested that the thermoplastic flow properties are similar at high temperatures.

Binder Concentration

Gloss is known to decrease with the addition or increased concentration of any binder. Webber(12) showed that gloss decreased with increased natural binder content, but modified starch gives about four points higher gloss than protein at a given concentration. Gloss decreased with increased latex addition until 40% and then increased at a similar rate.

Film Shrinkage

Lee(4) found that the gloss of a coating is proportional to the amount the film shrinks upon drying. He also showed that film shrinkage is proportional to the relative pore volume. The film shrinkage of a styrene-butadiene latex decreases with an increase in styrene content. The film shrinkage of any styrene-butadiene binder is less than a

natural binder. Protein has the highest film shrinkage which is consistent with its low gloss development.

Drying Temperature

This information led to another study by Lee(9) which concerned the effects of drying temperature on gloss. He found that a change in temperature below the minimum film forming temperature (MFFT) or above the glass transition temperature (Tg) did not affect the gloss. Only in the range between the MFFT and the Tg did changing temperature affect gloss. Gloss fell rapidly after the MFFT until the Tg was reached. This range has been called the gloss transition temperature. Lee also found that the MFFT and Tg increased with increasing styrene content. Gloss is highest below the MFFT, but the binder has no binding strength. If the coating could be dried within this temperature range, you would have limited coalescing of the binder. This would, in theory, allow you to dry a sheet at the proper temperature to minimize the loss in gloss and still have sufficient binding.

This theory has no applicability with currently marketed latexes because of their low MFFT, but it led to experimentation directed at developing new latexes called "composite latexes". Composite latexes are made by covering a high styrene or polystyrene seed with a layer of softer styrene-butadiene latex. Dow claims that the hard core of the particle limits the deformability to allow limited coalescing at a wide range of temperatures, but they are still in the experimental stage.

Affect on Packing

The loss of gloss with addition of binder to an all clay coating has earlier been attributed to a lesser degree of pigment orientation caused by interference of the binder. This however, has not been found to be true. Lapoutre(6) found that the addition of latex does not significantly change the degree of orientation. However, he did find that it affected the packing structure of the clay. The plot of coating thickness versus latex content increased rapidly at lower content then more gradually as content increased. This plot resembles a theoretical plot using the assumption of microdomains which supports Hagemeyer's(21) results. He concluded that when rhombi are added to plates they tend to separate into plate-rich and rhombus-rich domains.

Particle Size

Studies of the effect of latex particle size on gloss indicate that the effect might be linked to the absorbancy or porosity of the substrate. Lee(4) and Miller(11) agreed that on a nonabsorbant substrate such as polyester or mylar, gloss decreases with increasing particle size. But Miller found that for a paper substrate, gloss increases with increased particle size.

APPLICATION VARIABLES

Coat Weight

Gloss increases with increasing coat weight then levels off to a maximum attainable gloss for that particular system (4,7) Kaliski(2) found that the most dramatic change in gloss occurred between 4 and 5 g/m^2. This indicates that 5 g/m^2 is probably the minimum coat weight required to effectively cover the fibers.

Critical Pigment Volume

Webber(12) showed that gloss decreased with increasing CPV for natural binders. The minimum gloss reading was obtained at or close to the critical pigment volume content.

Dispersants

The effect of a dispersant on the gloss of a coating as described by Lee(4) is to increase gloss to a point of maximum dispersion then decrease at a similar rate. Flocculation or destabilization of suspended particles was found to lead to a more porous coating.

Binder Migration

Heiser and Cullen(15) showed that the binder does redistribute itself in the sheet and that the two major factors affecting binder migration are the percent solids of the coating and the rate of drying. The lower the solids the greater the migration of the binder. Fast drying results in a binder-rich surface. They also found that smaller particles appear to migrate less. Heiser and Baker(13) then studied the

effect of binder migration on gloss. They could not prove that the presence of binder at the surface adversely affected calendered gloss.

Substrate Absorbancy

Absorbancy can affect both composition and structure of a paper coating, particularly with quick dewatering(14). Higher absorbancy gave lower gloss. The effect of absorbancy is lessened by higher coat weight of higher coating solids. The absorbancy of the substrate draws the binder away from the surface. Water retention agents help the nullify the effect of absorbancy. Quick dewatering gives lower gloss, because the particles have less time to orient themselves.

Drying Conditions

Gloss decreases with increasing drying rate(15). This agrees with Lapoutre(14), who concluded that quick dewatering adversely affects gloss. However, Hershey(20) found that after the supercalender, the fast dried paper gave highest gloss. The affect of drying conditions receedes at higher coat weights(7). Lee(4) found that on an ideal substrate, gloss was only very slightly affected by the drying temperature.

SURFACE PROPERTIES

Smoothness

Gloss and surface smoothness are very closely related. In fact, many of the authors surveyed used the terms interchangeably. The smoothness of a coating has been found to

exist on two levels(18,2). The term macrosmoothness (or roughness) is used to describe the hills and valleys in the coated surface. These irregularities are on the order of 10-20 microns. Microsmoothness is caused by sharp edged depressions produced by irregular collapses which take place during the final drying stages. These disturbances are on the order of one micron in size. Macrosmoothness can be changed relatively easily by calendering. Microsmoothness, although slightly changed in calendering, is mostly controlled by wet coating characteristics. Coating microsmoothness decreases with the addition of latex(6). It changes sharply with small additions of latex, then only changes slightly after that. The addition of latex creates irregular stressts in the coating. Kaliski(5) found that gloss is inversely proportional to surface stress concentration. Gloss has been found to be correlated to the square of the microsmoothness(1).

According to the Fresnel theory, the specular reflectance of an optically smooth surface is a function of the refractive index and the angle of incident light. According to the Chanmayanandam theory for the specular reflectance of a rough surface, specular reflectance is a function of the angle and wavelength of incident light as well as the roughness. Lee(4) combined these two equations and used the resulting equation to calculate the Tappi gloss for many materials used in coating. The results showed that any single material can be developed to 100% gloss. This indicates that the loss of gloss of a coat-

ing is probably due to structural changes due to mixing different particles.

Porosity

The specular reflectance of light takes place if the irregularities in the surface do not exceed 1/16 the wavelength of the incident light(5). This indicates that not only the pore volume but also the relative pore size also affects the gloss. Gloss increases with decreased pore volume(22). Average pore size decreases with decreased particle size(17) and with the addition of a soluble binder(3). The effect of a change in mean pore size is unclear because of the probability of a corresponding change in pore volume. If Kaliksi's statement about the effect of the size of the irregularities on gloss is accepted, gloss should increase with decreasing pore size.

Scattering Coefficient

Trader(3) showed that gloss increased with a decrease in scattering coefficient. The addition of a binder to a particle system can either increase or decrease depending on the particle size. For coarse particles, the addition of a binder decreases scattering, but for small particles, the addition of a binder causes a change in the effective particle size and distribution which decreases gloss. Lapoutre(14,6) found that light scattering decreases with increased calendering. This effect is more prominent at higher nip pressures. He theorized that the dispersed air voids are probably the scattering sights. Latex addition increases scattering up to 15-20%

binder which supports the theory of latex particles acting as spacers between pigment particles.

Lapoutre(6,18,19) and Kaliski(5) have shown a close, almost linear correlation between light scattering and porosity.

FINISHING CONDITIONS

Gloss increases exponentially with calendering so that gloss increases less with each additional nip(17). For each binder level there is a certain level of gloss attainable which is independent of further finishing(5). Gloss due to calendering increases with increased calender temperature, increased moisture content(11), and increased nip pressure (8,19). Munch, Schlunk, and Schmitz(19) found that nip pressure and calender temperature are interdependent so that a set standard for gloss can be maintained with reduced nip pressure if the paper is calendered at a proportionally higher temperature. Supercalendering increases the small to large void ratio(18). Paper gloss was raised from 45-70% just by rubbing the sheet. This could mean that the brushing action of calendering affects this microsmoothness and the pressure affects the microsmoothness.

EXPERIMENTAL DESIGN

This experiment was designed to study the effects of substrate porosity and drying method on the surface properties of the final coated sheet. Four different substrates were used. A mylar sheet was used as a zero porosity substrate. The other three sheets were Millipore filter papers with .22,.45, and .80 micron average pore sizes respectively. The Millipore filter paper was used because it has a pore structure similar to paper, the average pore diameter has a very small standard deviation, and it is almost completely nonabsorbant. Three different coatings, each with a different binders, were applied to the sheets via drawdowns with a Meyer rod. The binders used were an acrylic latex (Rohm Haas B-15), a polyvinyl acetate latex (National 1105), and a styrene butadiene latex (Dow 620). Three different drying methods were used. One set of sheets was back dried on a hot plate at 190 °F. Another set was blown dry from the top with hot air. The third set was allowed to air dry.

A total of 99 sheets were coated. A #13 Meyer rod was used and it gave an average of 24g/m² or 16 lb/24" x 36" ream. Coatings were made up with a #1 high brightness clay (Hydrafine 90) with 18 parts

binder, .3 parts CMC 7M, and .5% Dispex. Coatings were applied at 55% solids. The Brookfield viscosities of the coatings were the same. For each drying method, three sheets were coated with each coating. The coated sheets were conditioned in a constant humidity room. Gloss, smoothness, K&N ink holdout, and Hercules sizing were tested before and after calendering. For ease of discussion, I will discuss the effects of pore size, drying method, and binder type together.

DISCUSSION AND RESULTS

Gloss

The gloss of all uncalendered sheets increased linearly as the average pore size increased from .22 to .80 microns regardless of binder or drying method (Fig. 1). For all coatings and drying methods, gloss increased between 3 and 4%. The coating made with styrene butadiene gave the highest gloss for all drying methods. The acrylic latex coating gave the lowest gloss. As for the effect of the drying methods (Fig. 1-5), the sheets that were blown dry had the highest gloss followed by air drying and then back drying. For styrene butadiene and polyvinyl acetate the blown dry gloss was 2-3% higher than the air dried gloss and 5% higher than the back dried gloss. For the acrylic coating, the blown dry gloss was 10% and 12% higher than air dried and back dried gloss respectively. After calendering the shape of the curves changed(Fig. 2). The curves are quadratic with a peak around .45 micron average pore size and the gloss at .22 and .80 microns is about the same. The effects of binders and drying methods are the same after calendering.

If you accept the theory that the binder migrates toward the heat source during drying, then the blown dry coatings would be binder rich. The back dried coatings

would be binder deficient and the binder in the air dried coating should be evenly dispersed. This would mean that the more binder you have at the surface, the higher the coating gloss.

Smoothness

Two methods were used to measure the surface smoothness of the coated sheets: the Parker Print Surf smoothness tester and the Sheffield smoothness tester. The Parker smoothness values were very low for both the uncalendered and the calendered sheets (Fig. 6).. Due to problems with the sheets bursting during testing, uncalendered smoothness was only measured for the blow dried set. For this set, the calendered sheets were slightly more smooth than the uncalendered sheets. Smoothness increased almost linearly as the average pore size increased for the styrene butadiene and polyvinyl acetate coatings, but the acrylic back and blow dried sheets smoothness was unaffected by a change in average pore size. Back drying gave the smoothest sheet and blow drying gave the roughest. The styrene butadiene gave the smoothest sheets and acrylic gave the roughest.

The Sheffield smoothness does not agree with the Parker smoothness (Fig. 7-9). The Sheffield smoothness values increased (smoothness decreased)

with increasing average pore size. The sheet also became less smooth after calendering. The roughness of all sheets increased by a multiple of 2-4. The uncalendered sheets were unaffected or slightly affected by a change in pore size. Styrene butadiene coatings had the smoothest surfaces but for uncalendered sheets smoothnesses were nearly the same. The difference came after calendering. The smoothness decreased with increasing average pore size. Back drying gave the smoothest sheet and air drying gave the roughest. You can't tell from these results if styrene butadiene or polyvinyl acetate gave the smoothest sheet.

The Parker smoothness is more related to gloss than is the Sheffield smoothness. Both methods agree that back drying gave the smoothest surface and that air drying gave the roughest. This indicates that a binder deficient surface is the smoothest and that a heterogeneous mixture of binder and pigment is rougher than a binder rich or pigment rich surface.

Porosity

The porosity of the coated sheets was too low for measurement by the Sheffield porosity meter. Since this was the only available method for measuring porosity, the effects of substrate porosity on the porosity of the coated sheet could not be studied.

Hercules Size

Because of the inability to measure the porosity, the Hercules size test was used to measure the ability of the caoted sheet to hold out a fluid. The uncalendered sheets held out the dye twice as long as the calendered sheets (Fig. 10-11). Before calendering the styrene butadiene blow dried sheets gave the highest sizing, but the styrene butadiene air and back dried gave the two lowest times. Back drying gave the highest sizing for polyvinyl acetate and the acrylic latex and blow drying gave the lowest in both. After the styrene butadiene blow dried sheets, the polyvinyl acetate had the highest uncalendered size then acrylic latex and styrene butadiene. The general trend for uncalendered sheets is slightly increasing Hercules Size with increasing average pore size. After calendering the sizing of the polyvinyl acetate sheets increased with increasing pore size, but for styrene butadiene and acrylic binders it decreased with increasing pore size. Polyvinyl acetate gave the highest calendered sizing and styrene butadiene gave the lowest. Again for styrene butadiene, blow drying gave higher sizing than back drying and it was the opposite for polyvinyl acetate and acrylic latex sheets.

I conclude that after calendering the coating structure is more open. Also, blow drying gives the tightest

packed structure for styrene butadiene, while back drying gave a tightly packed coating for polyvinyl acetate and the acrylic latex. The coating structure becomes more open as the substrate porosity increases.

Ink Holdout

The ink holdout was unaffected or slightly decreased with increasing average pore size (Fig. 12-16). For uncalendered sheets polyvinyl acetate generally gave the best ink holdout and styrene butadiene gave the worst. The exception is blow dried polyvinyl acetate which gave very poor holdout. As in Hercules size, the back dried gave the best ink holdout for polyvinyl acetate and acrylic latex, but blow dried gave the best holdout for styrene butadiene. The calendered sheets responded the same as uncalendered except that holdout slightly decreased with increasing average pore size between .22 and .45 microns then increased so that the .22 and .80 micron values were the same.

CONCLUSIONS

It was concluded that the styrene butadiene bound coating gave the highest gloss development and the smoothest sheet but the worst Hercules size and ink holdout. Polyvinyl acetate had the second highest gloss and smoothness and the highest sizing and ink holdout. The acrylic binder had the worst gloss development and smoothness and the second best Hercules size and ink holdout.

Blow drying gave the best gloss and worst smoothness for all binders. It gave low sizing and ink holdout for polyvinyl acetate and acrylic latex but high sizing and holdout for styrene butadiene. Back drying had low gloss but the best smoothness for all binders. Back drying gave the best sizing and ink holdout for polyvinyl acetate and the acrylic latex but not for styrene butadiene.

With increasing average pore size, the uncalendered sheets increased in gloss, Hercules size, and ink holdout, and the smoothness was unaffected. After calendering, the results were unclear with respect to pore size.

FIGURE 1

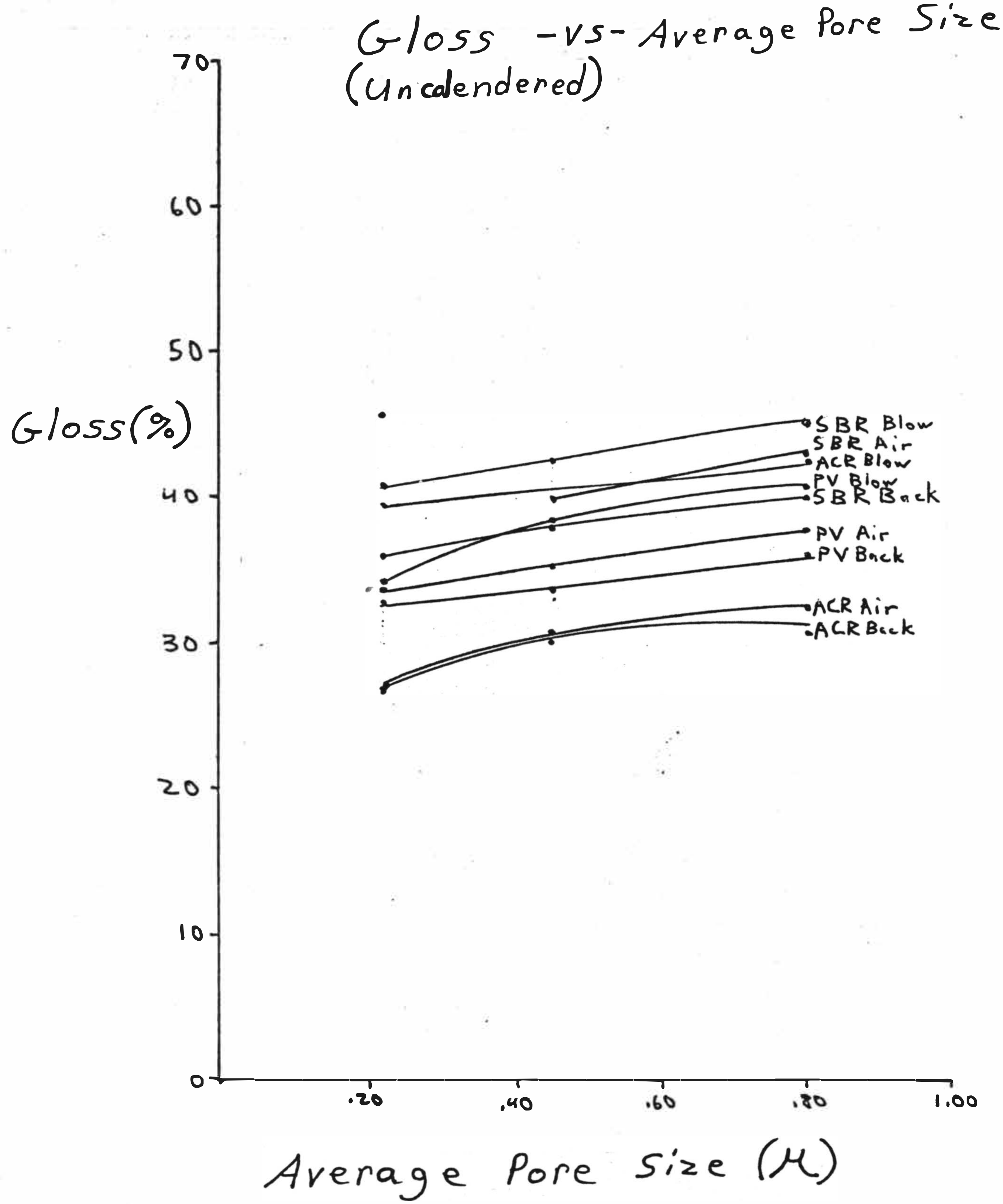
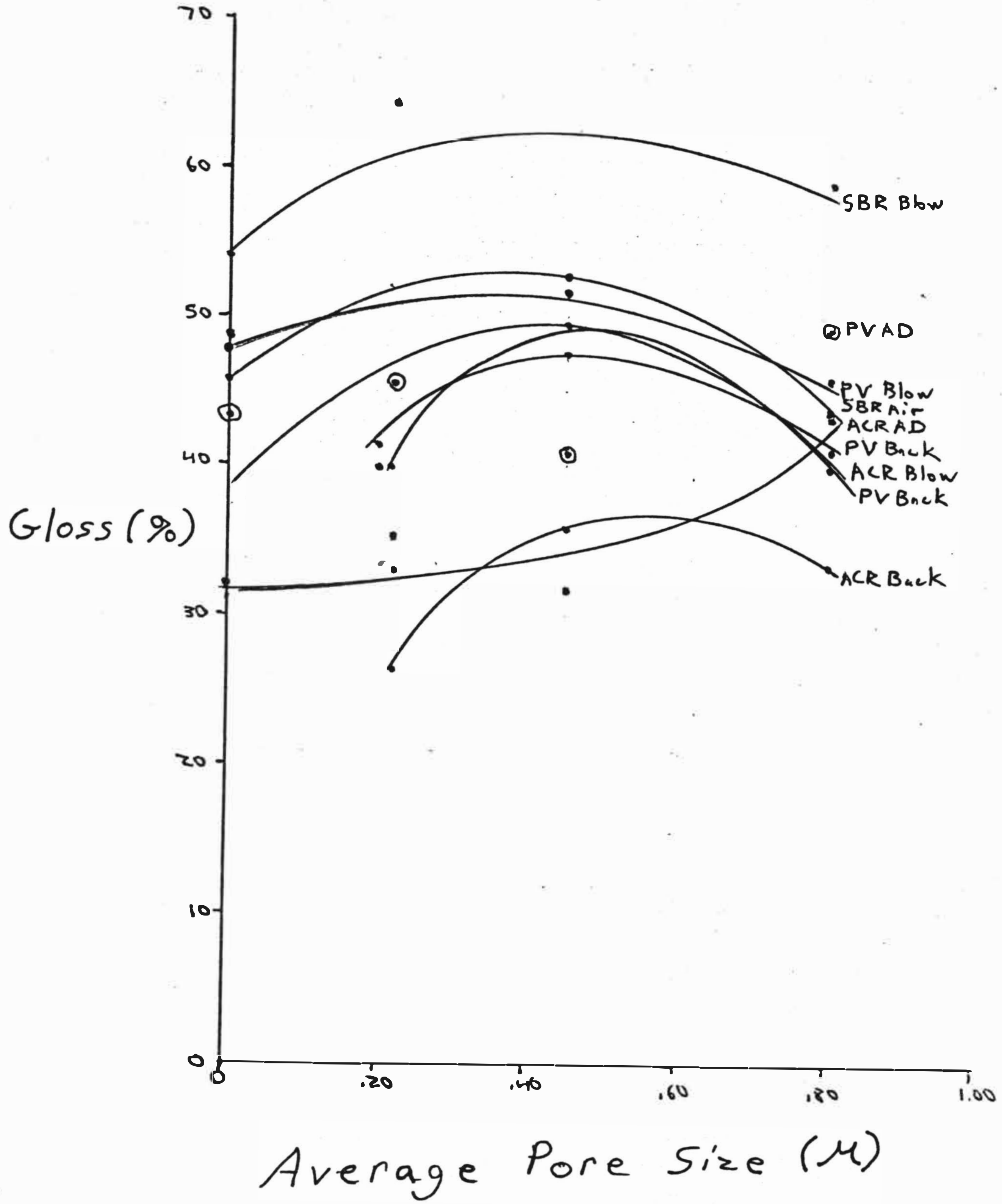
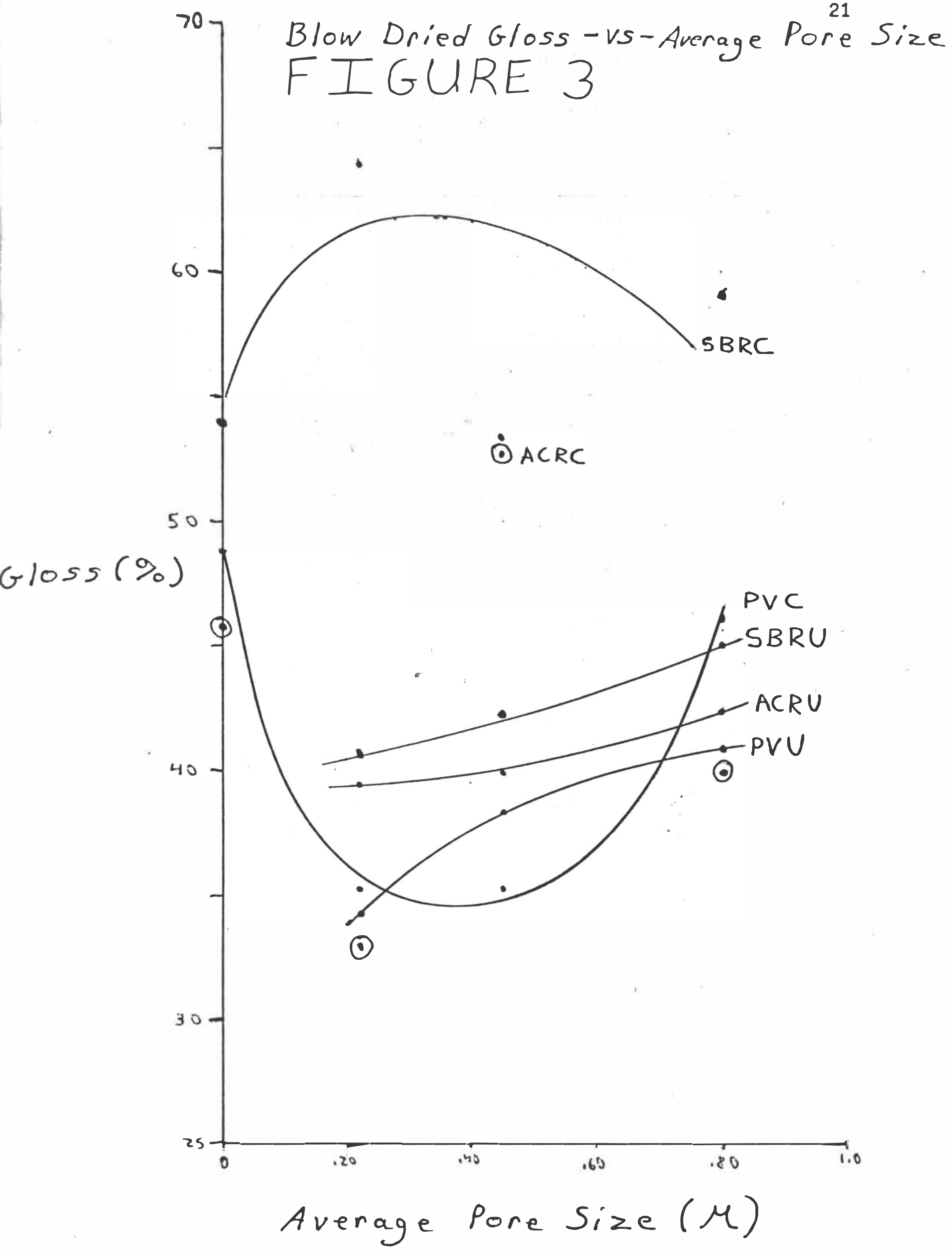

Gloss -vs- Average Pore Size
(Uncalendered)
Gloss(%)
70
60
50
40
30
20
10
0
.20
.40
.60
.80
1.00
Average Pore Size (μ)
SBR Blow
SBR Air
ACR Blow
PV Blow
SBR Back
PV Air
PV Back
ACR Air
ACR Back

FIGURE 2

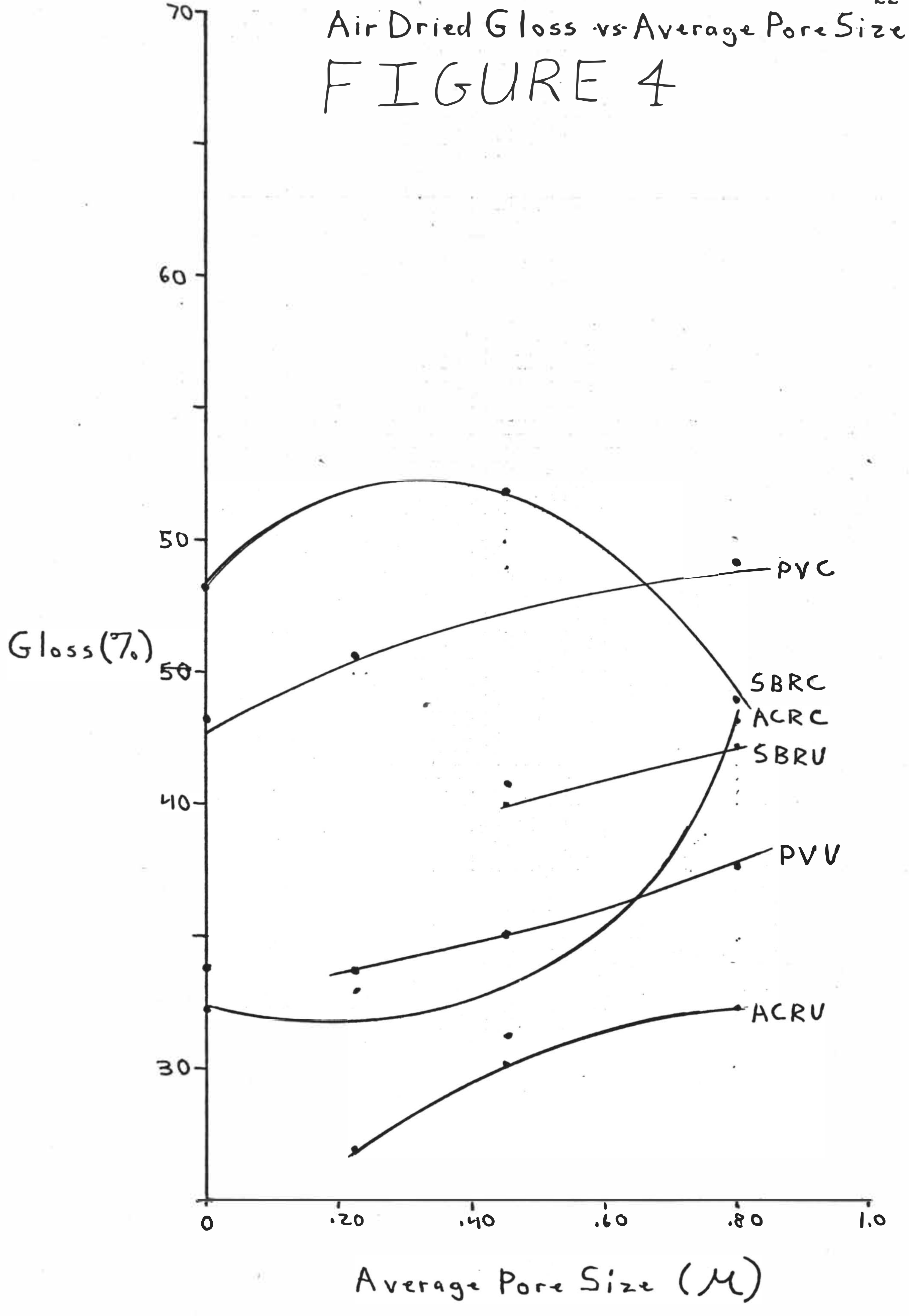
Gloss -vs- Average Pore Size (Calendered)




Blow Dried Gloss -vs- Average Pore Size
FIGURE 3
70
60
50
40
30
25
Gloss (%)
SBRC
ACRC
PVC
SBRU
ACRU
PVU
0
.20
.40
.60
.80
1.0
Average Pore Size (μ)

Air Dried Gloss vs Average Pore Size

FIGURE 4



Back Dried Gloss -VS- Average Pore Size

FIGURE 5

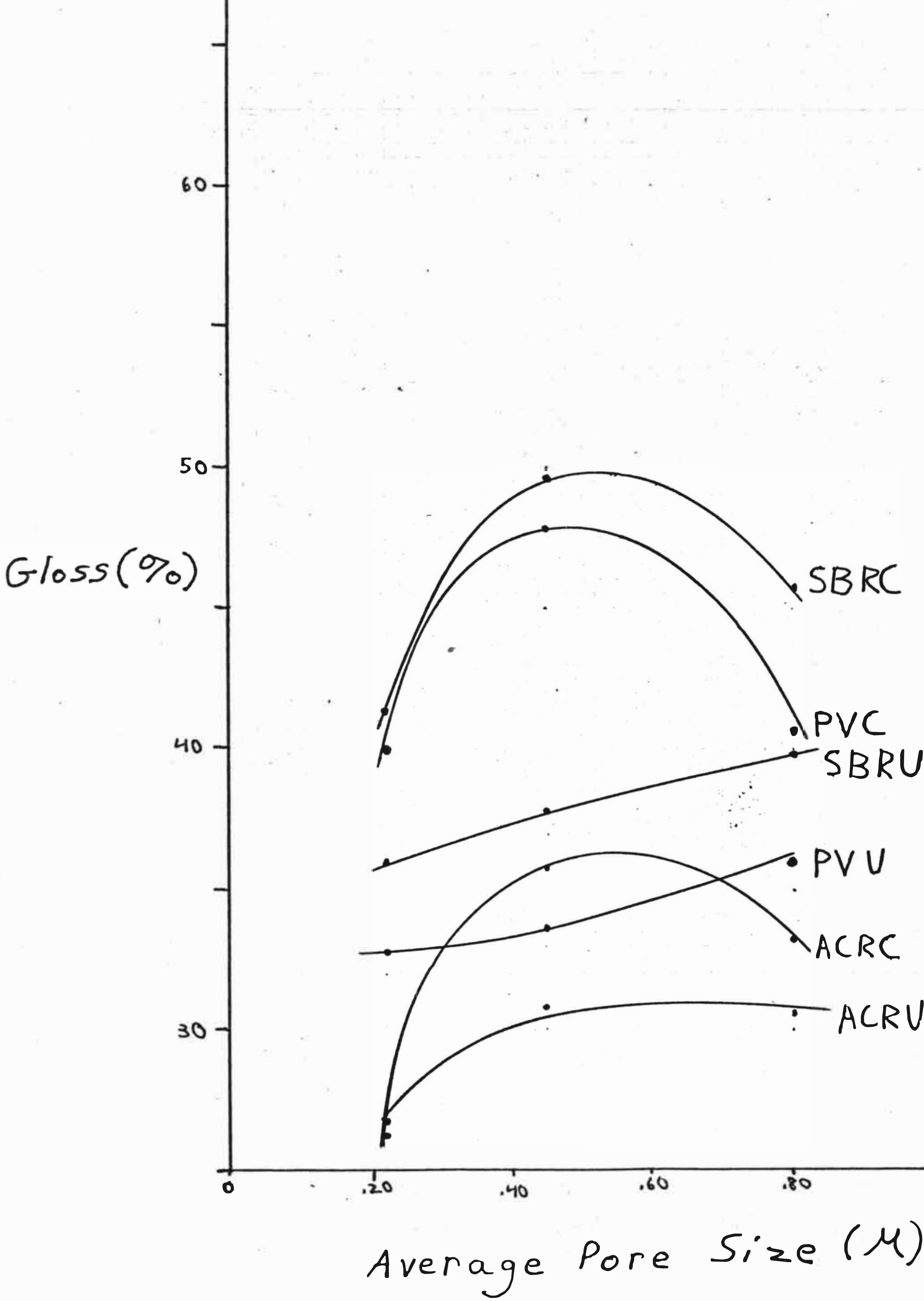


FIGURE 6

Parker Smoothness -VS- Average Pore Size

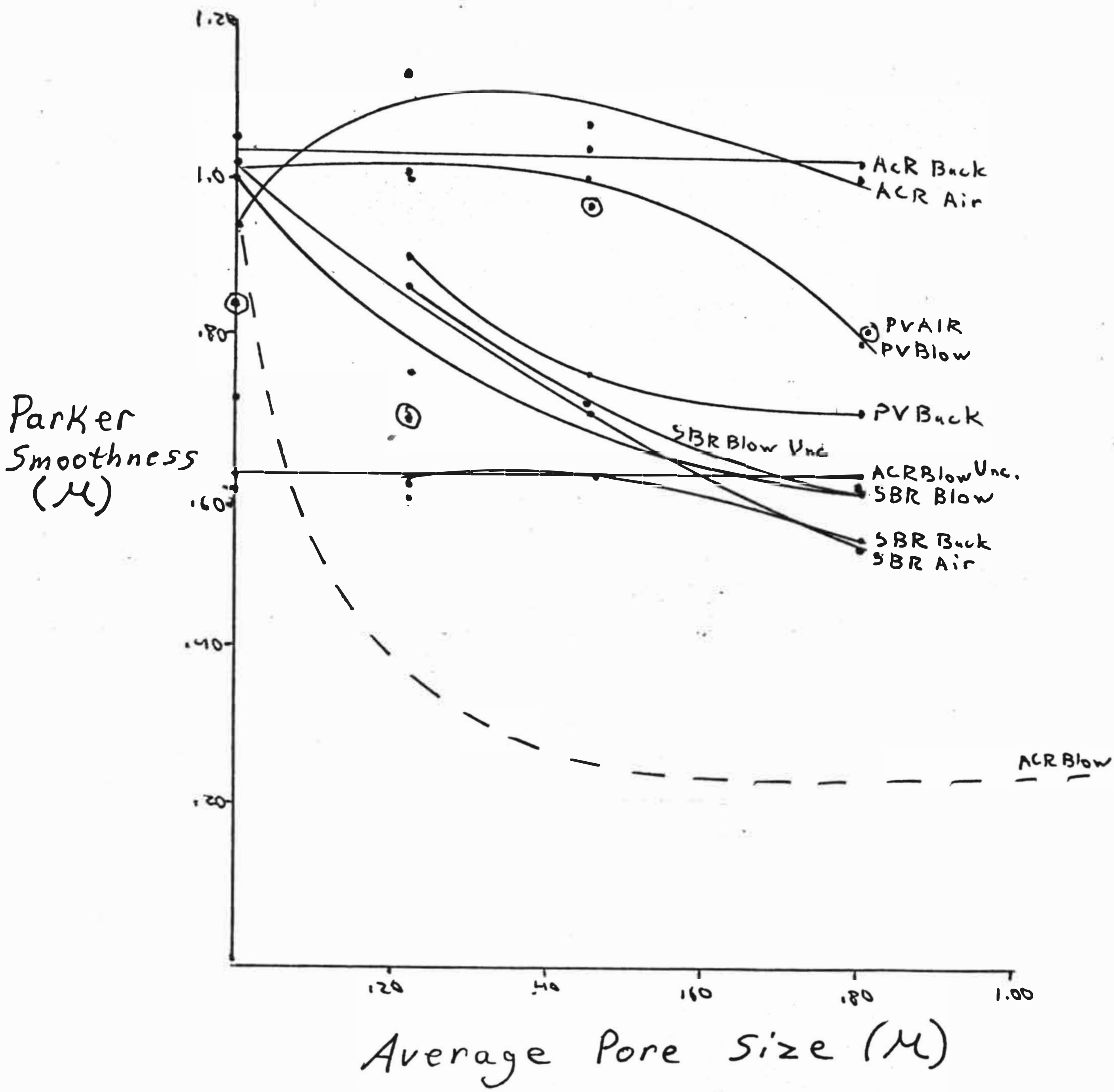


FIGURE 7

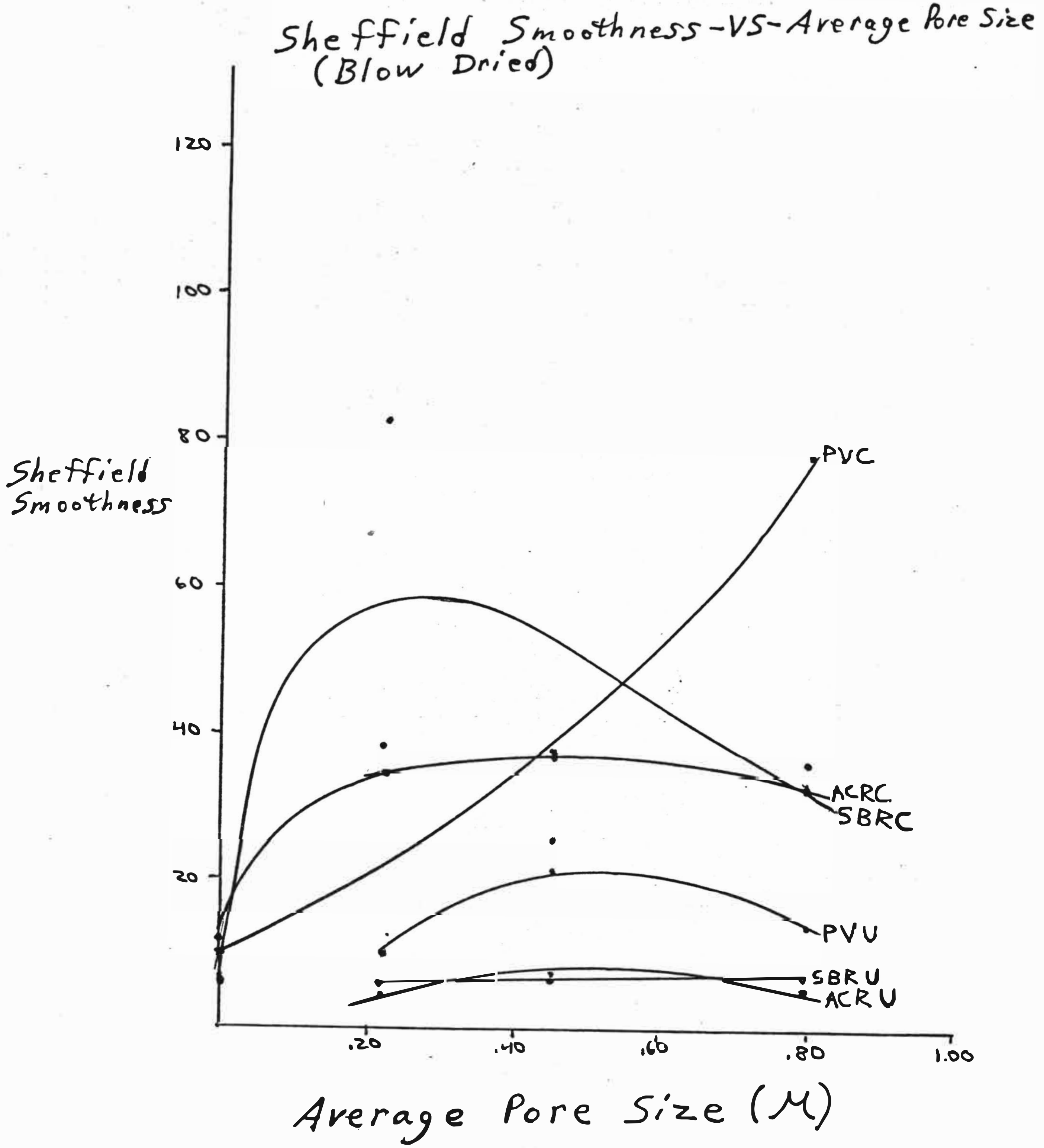

Sheffield Smoothness -VS- Average Pore Size
(Blow Dried)
120
100
80
60
40
20
Sheffield Smoothness
PVC
ACRC
SBRC
PVU
SBRU
ACRU
.20
.40
.60
.80
1.00
Average Pore Size (μ)

FIGURE 8

Sheffield Smoothness -VS- Average Pore Size (Back Dried)

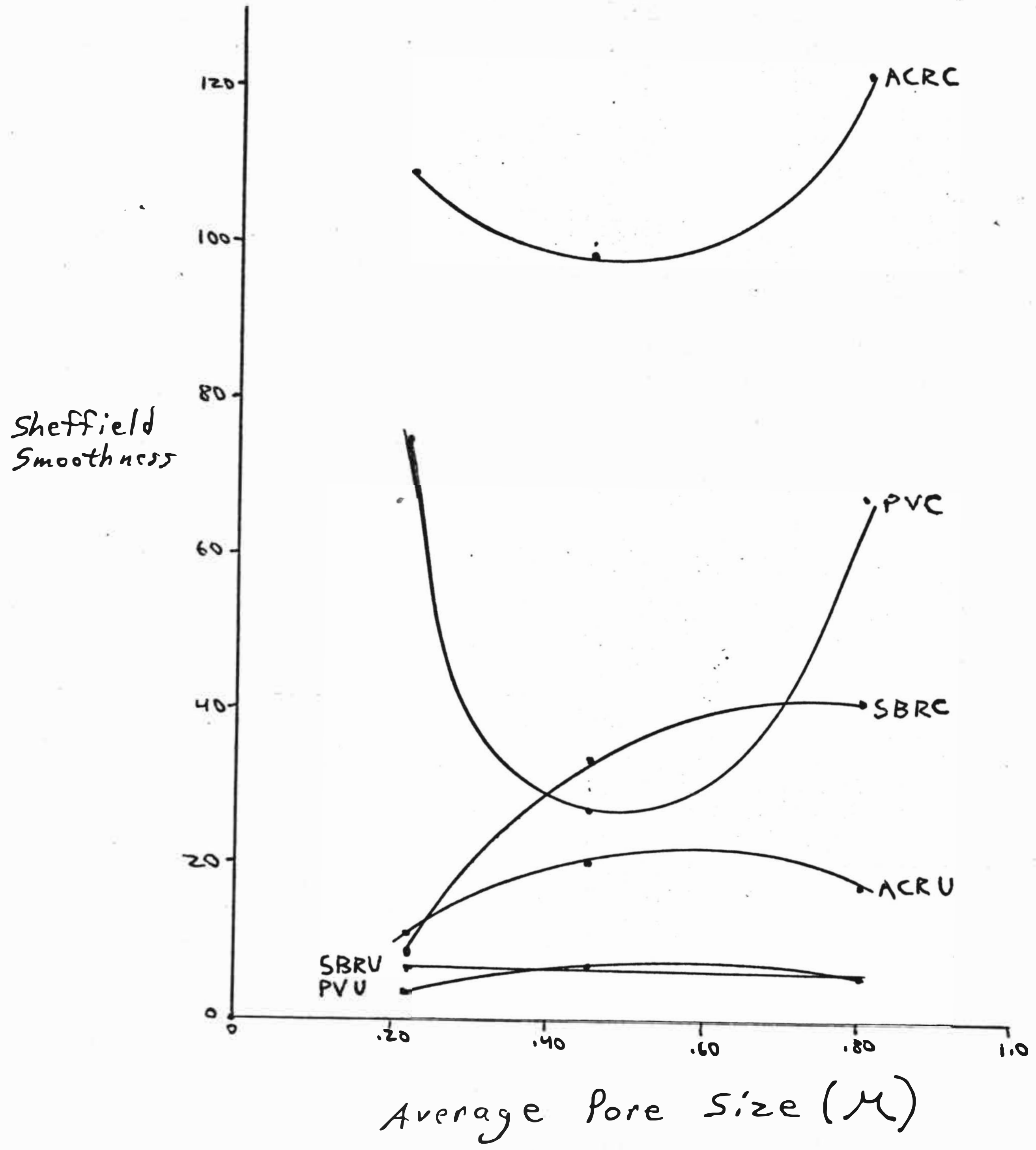


FIGURE 9

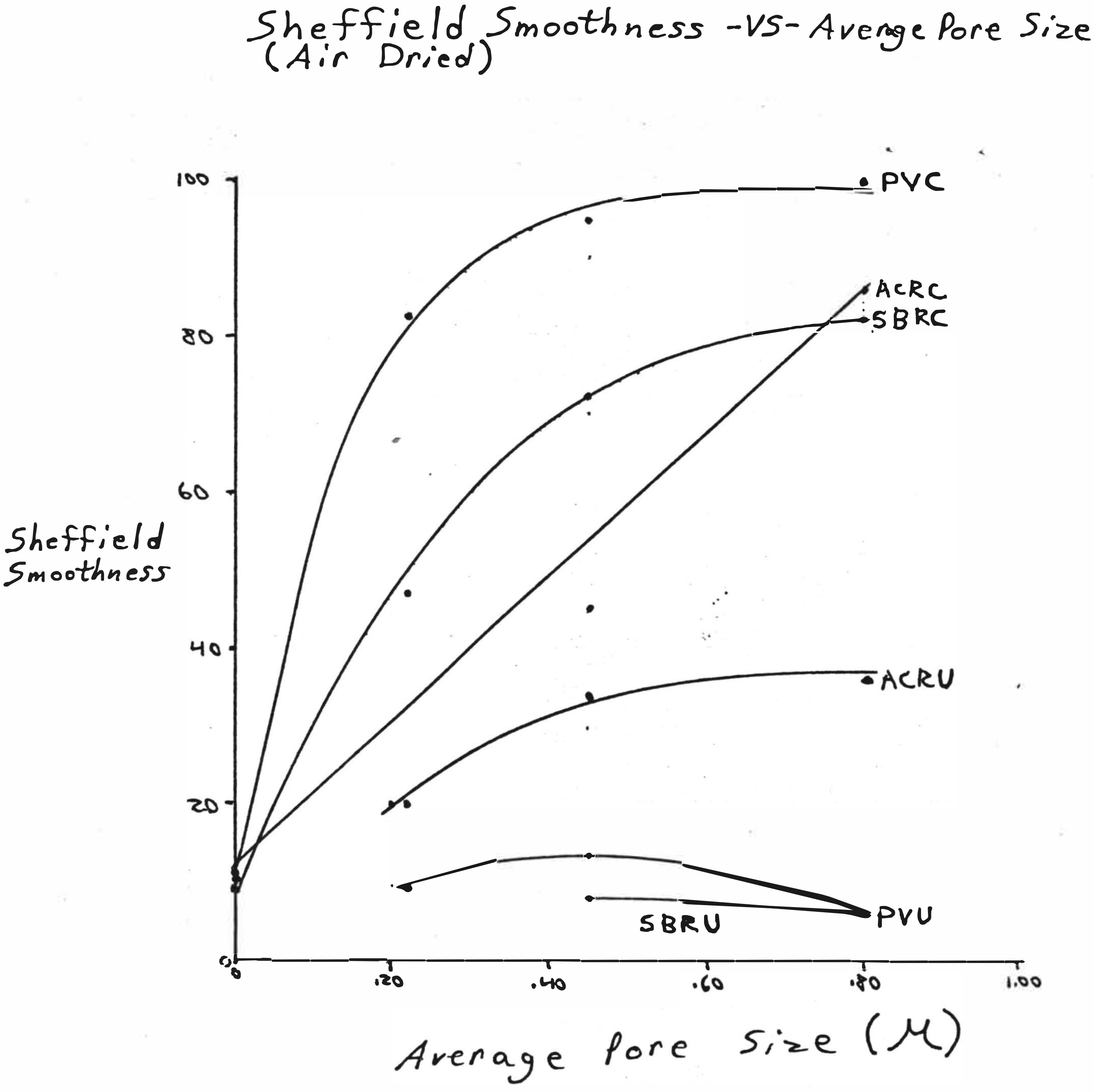

Sheffield Smoothness -VS- Average Pore Size
(Air Dried)
Sheffield Smoothness
100
80
60
40
20
0
0
.20
.40
.60
.80
1.00
Average Pore Size (μ)
PVC
ACRC
SBRC
ACRU
PVU
SBRU

FIGURE 10

Hercules Size -vs- Average Pore Size (uncalendered)

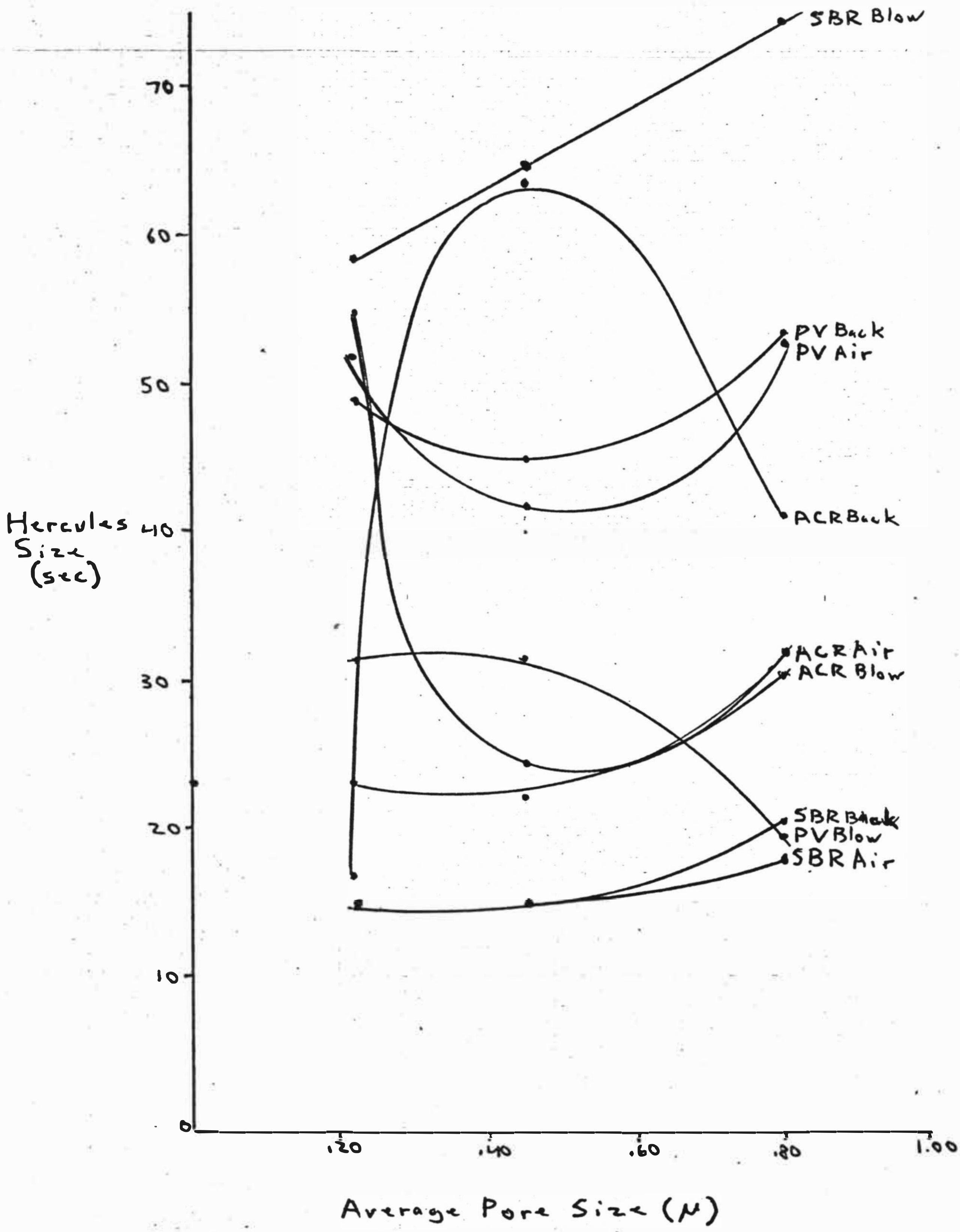


FIGURE 11

Hercules Size -vs Average Pore Size (calendered)

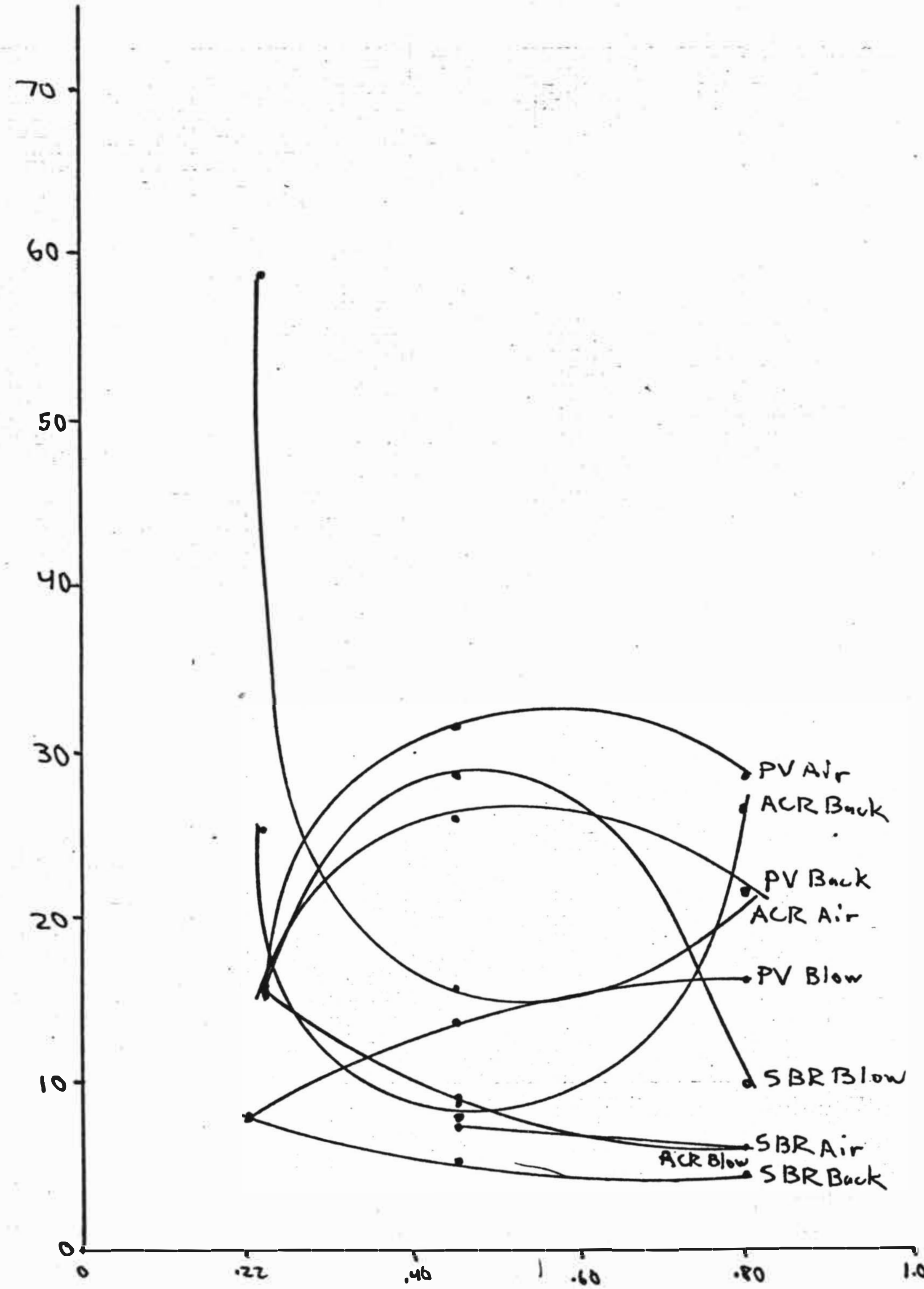


FIGURE 12

K&N -vs- Average Pore Size
(Uncalendered)

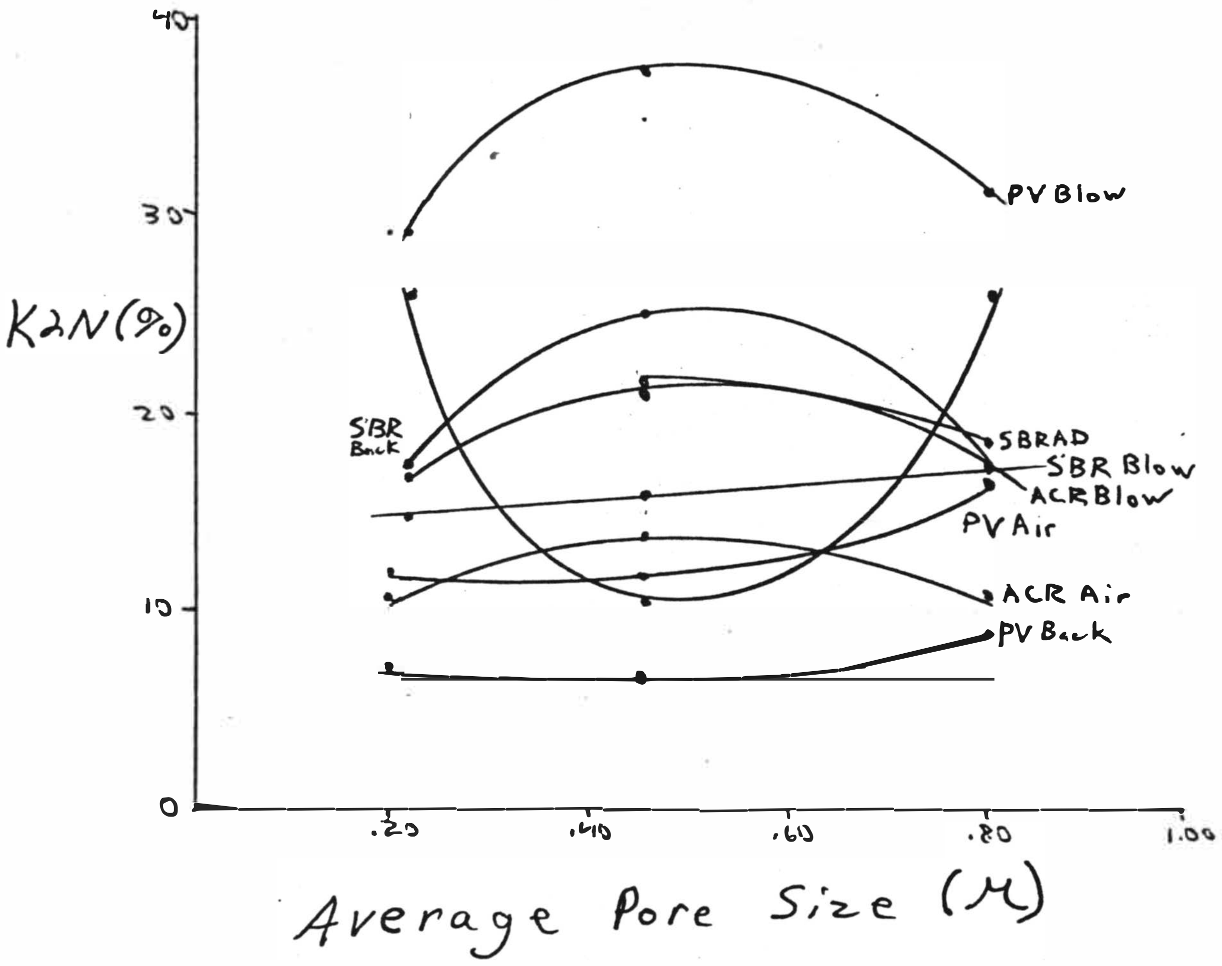
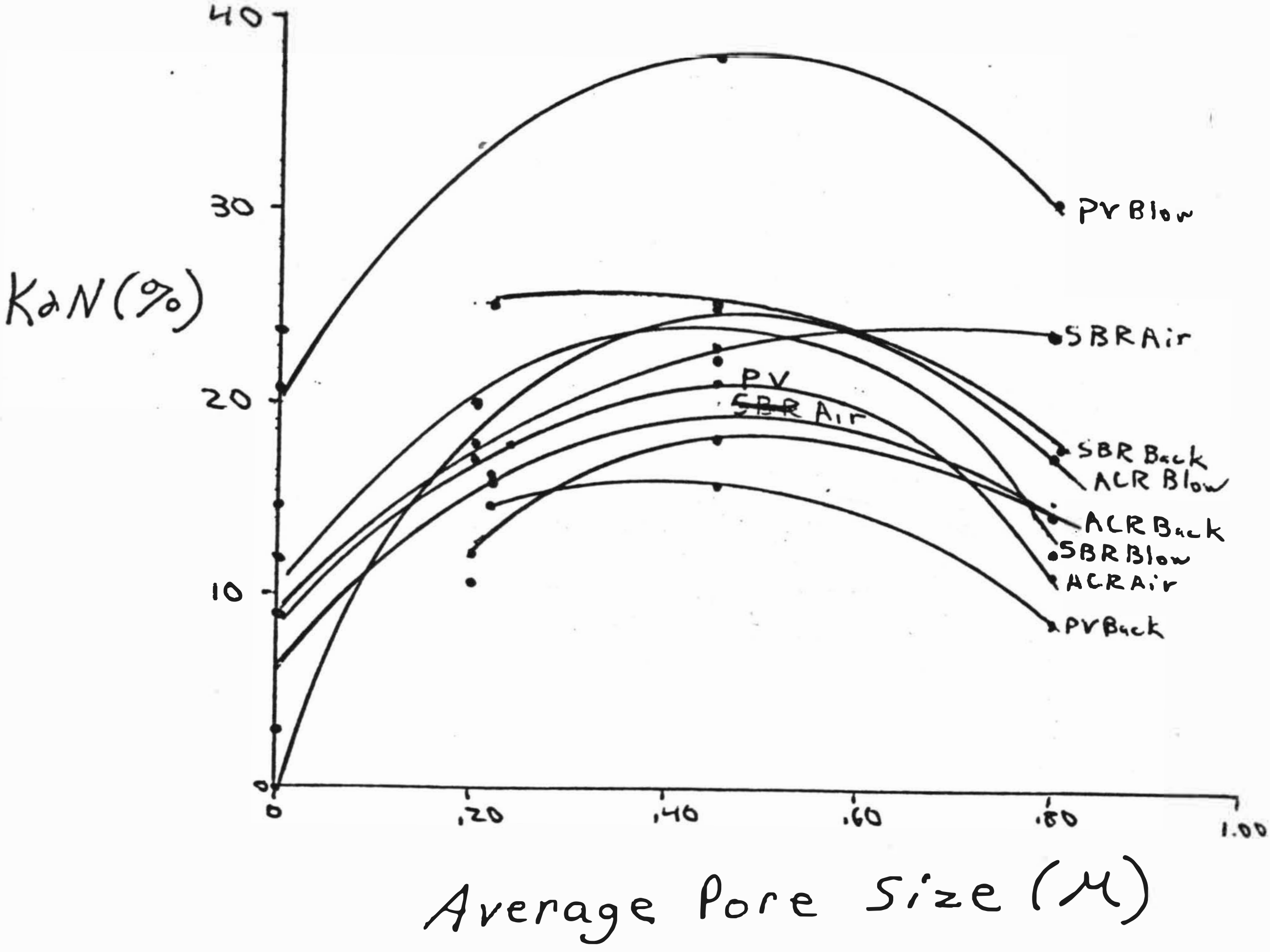
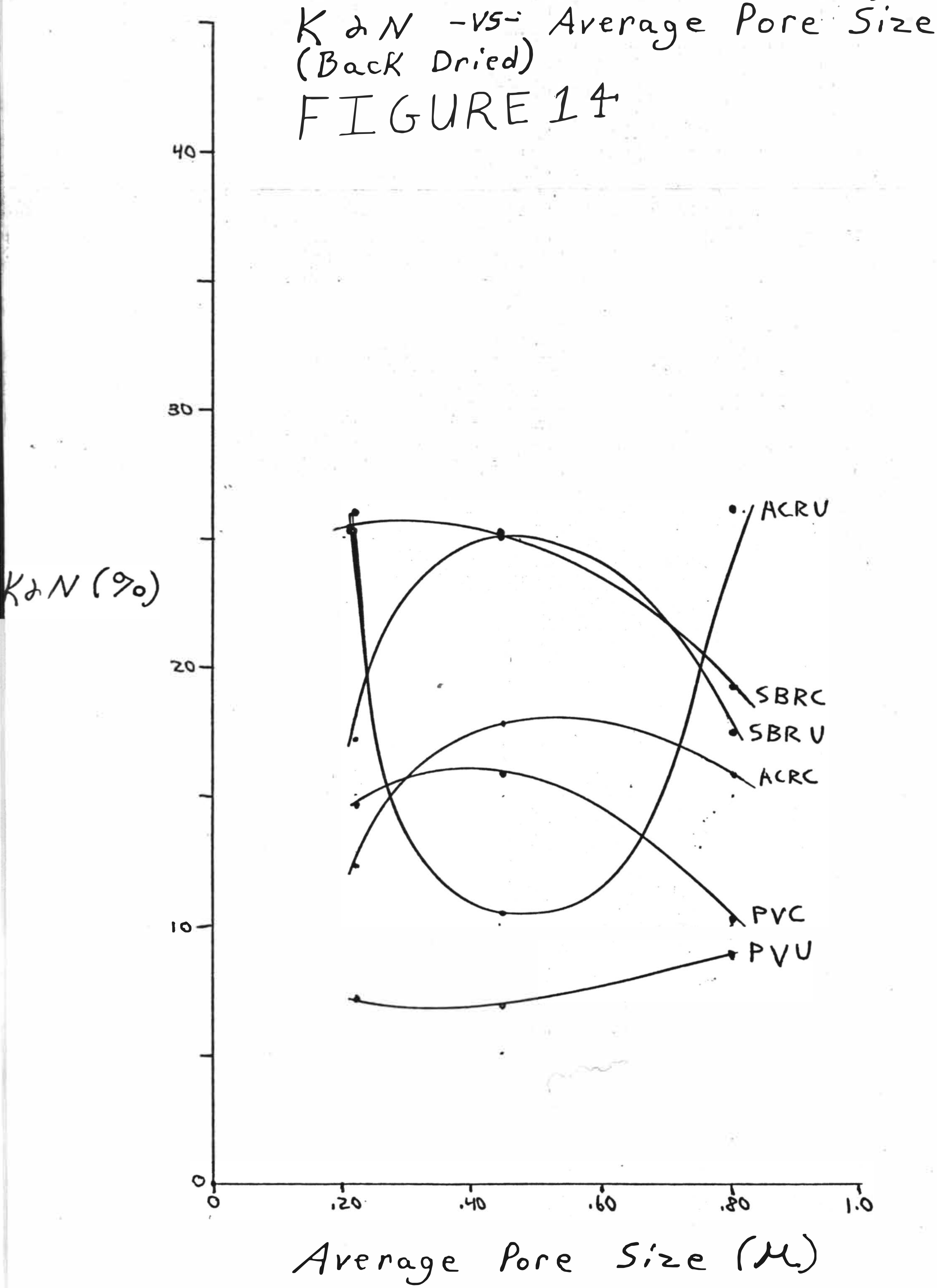


FIGURE 13

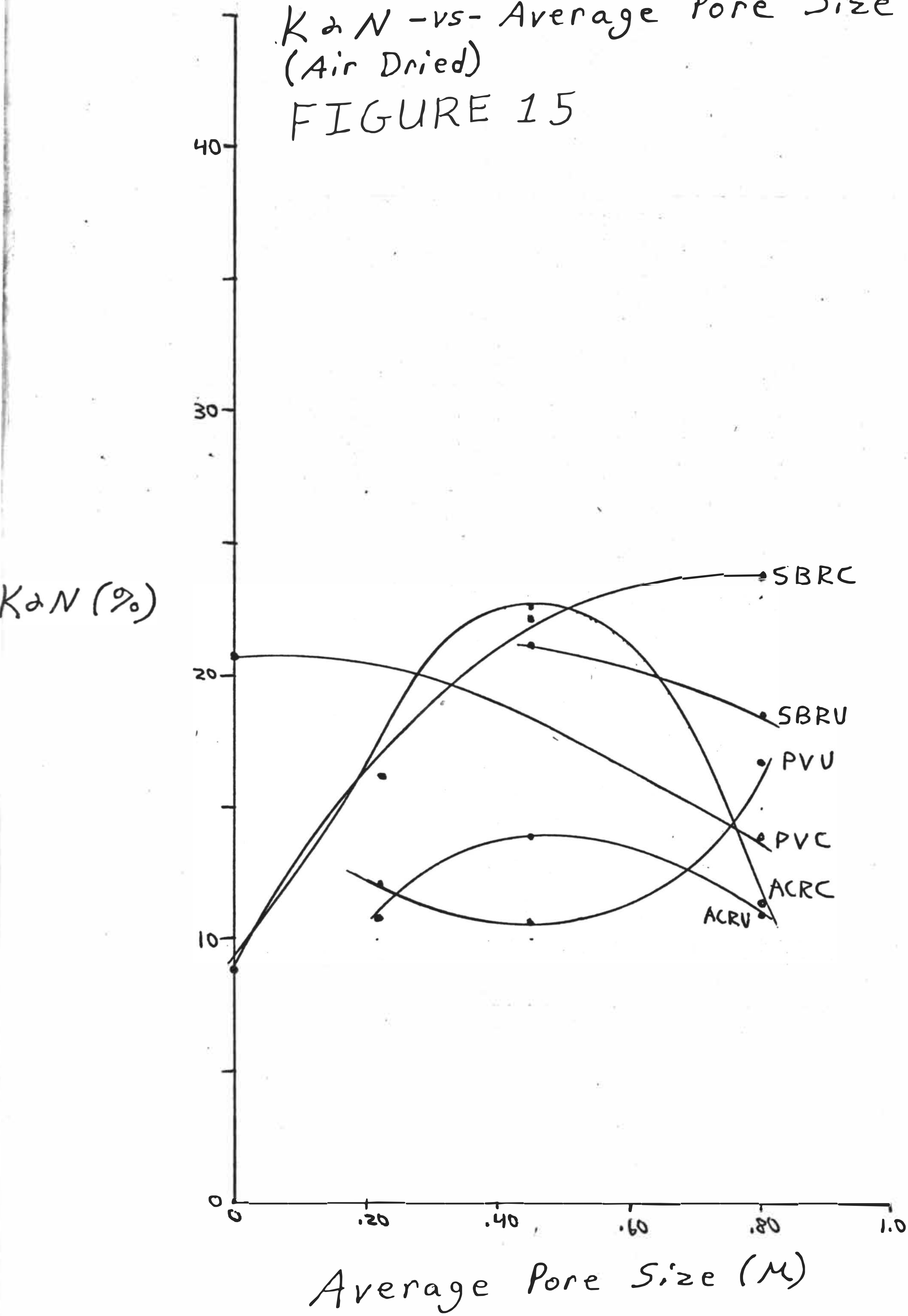
K&N -vs- Average Pore Size (calender)




K & N -VS- Average Pore Size
(Back Dried)
FIGURE 14
K & N (%)
0
10
20
30
40
0
.20
.40
.60
.80
1.0
Average Pore Size (μ)
ACRU
SBRC
SBRU
ACRC
PVC
PVU

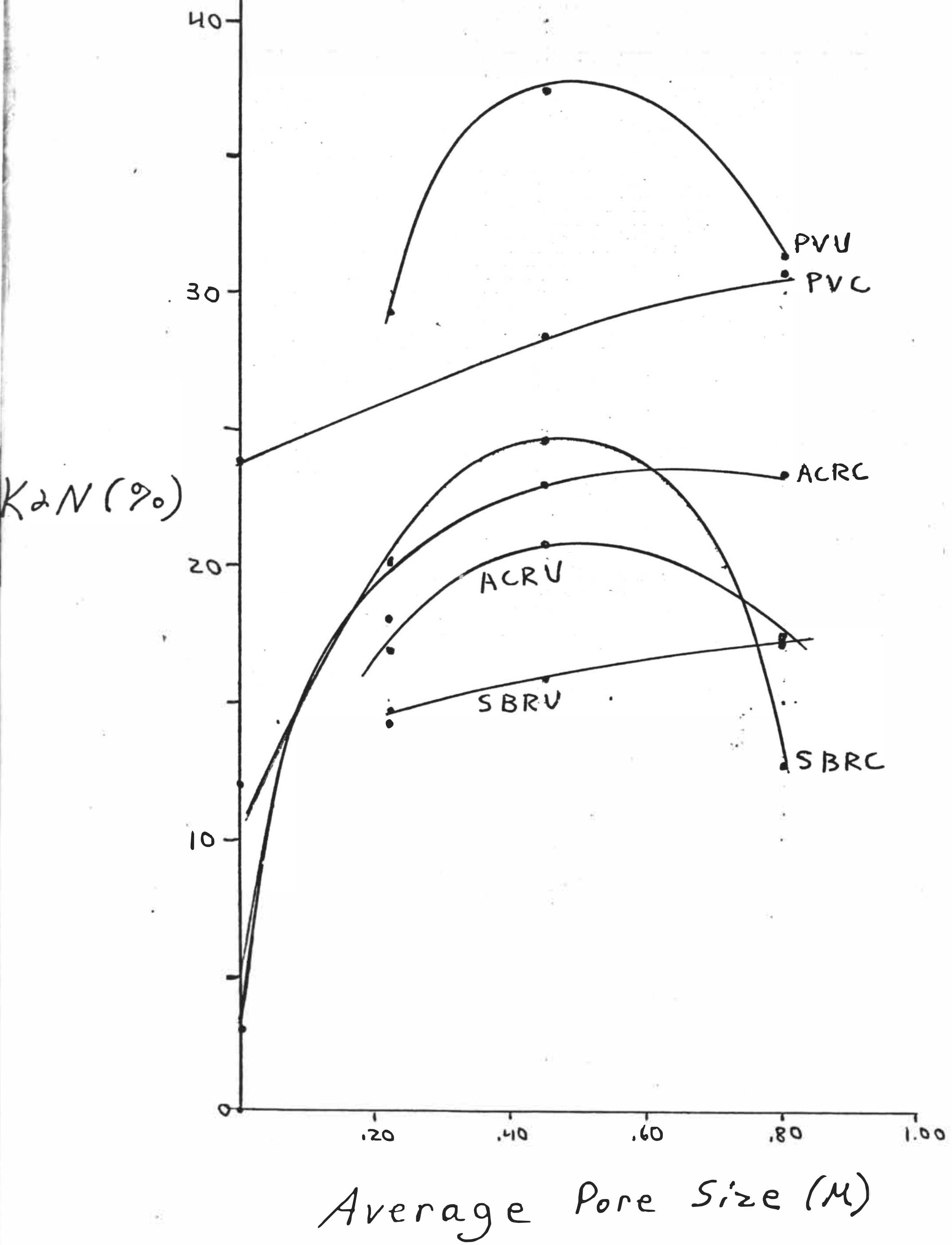
K∂N -vs- Average Pore Size
(Air Dried)

FIGURE 15



Kα N -vs- Average Pore Size (Blow Dried)

FIGURE 16



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