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Hydrogen Ion Concentration of Sheet Making Water and Its Relationship to the Hygroexpansion of Paper

by

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Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

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Abstract

The hygroexpansivity of paper is of particular importance in the paper industry. As paper dimensions become more critical, the problem of hygroexpansivity in paper necessarily becomes more critical. Since the hydrogen ion concentration (pH) of papermaking water effects the use of fillers, dyes, size, and the quality of the final product, the relationship between hygroexpansivity of paper and the pH of papermaking water is, therefore, an important consideration. Fortunately, the experimental evidence from this project indicates that the pH has little effect upon the hygroexpansion of paper. But rather, this project found the sheet density to have a far greater impact upon the hygroexpansion of paper.

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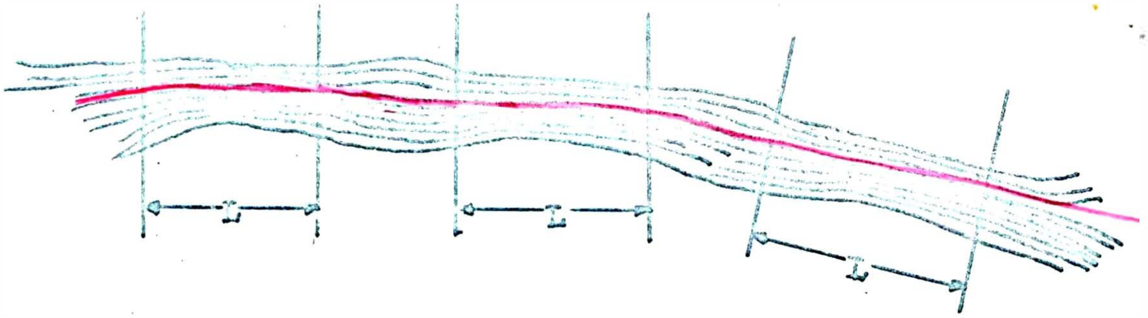
The phenomena of hygroexpansion in paper is of particular importance to the paper industry. Generally when the enviromental humidity is altered, a change in the sheet dimension is realized. As a result of this dimension instability with humidity change, major problems develop in the manufacturing, conversion, and end use of paper products. This project, therefore, is designed to isolate the effect that the hydrogen ion concentration (pH) of the sheet forming water exhibits upon the hygroexpansion of a handsheet. The time of fiber exposure with the hydrogen ion concentration was also varied to investigate its possible effect upon sheet hygroexpansion.

To fully understand hygroexpansion of paper, it is imperative first to develop a better understanding of the finer structures involved in dimensional changes. In simple terms, the cellulose fiber must be considered composed of macromolecules with a varying degree of packing. In regions of high packing order, molecules are held together by hydrogen bonds between cellulose hydroxyl groups. As order decreases, the number of hydroxyl groups involved in hydrogen bonding decreases. These large number of cellulose hydroxyl groups not involved in hydrogen bonding can then be considered as free or accessible(1).In the following diagram, the lengths (L) are the more ordered regions of the cellulose chain. In the regions between the crystalline regions, hydroxyl groups are readily accessible for combination with water vapor molecules.

Figure 1

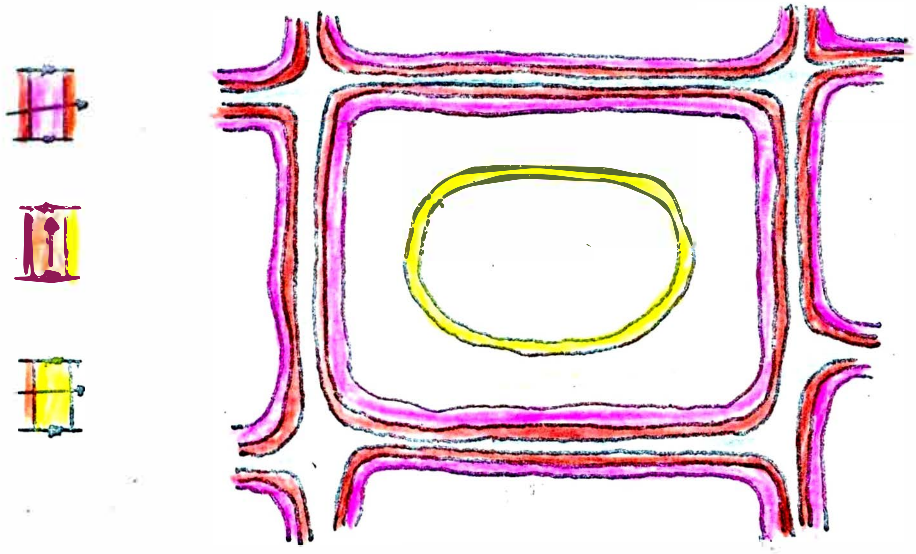


Cellulose Chain Passing Through Several Crystalline and Amorphous Regions (2)

Another important consideration in the explanation of hygroexpansion is the chemical and physical nature of the paper fiber cell walls. With maturing, the primary cell wall acquires large deposits of lignin; thus giving it very little swelling ability.(3) While seeming to have little ability to fibrilate, the primary cell wall is quite permeable to water. The fibril orientation is quite random and the wall itself is brittle and inflexible leading to cracking during beating. This cell wall then demonstrates a dual characteristic. While at first cellulosic, it gradually becomes more lignin like at maturity.(4)

Composed of two interpenetrating systems, cellulose and other polysaccharides and lignin, the secondary cell wall is a closed structure with no gaps or zones of weakness or detached fibrils. There are, however, varying degrees of lignin composition. These varying lignin contents are arranged in somewhat concentric rings of greater and lesser lignin content. A difference in the orientation of the crystallite chain molecules divides the secondary cell wall into three separate layers. The outer and innermost layers both uniformly thin, have the orientation of the chain perpendicular to the fiber axis. The middle layer, nearly parallel to the fiber axis, varies widely in thickness. Evidence indicates that a skin substance encloses every layer and fibril in this cell wall. (3) However, lignin content in this cell wall varies from softwood to hardwood. In softwood, a coherent structure of lignin is indicated while in hardwood the structure seems to vary depending

Figure 2



Typical Fibrous Wood Cell in Tranverse Section (3)

🟦 True middle lamella or intercellular substance

🟥 Primary cell wall

🟪 Outer secondary cell wall

🟧 Central secondary cell wall

🟨 Inner secondary cell wall

upon the lignin content. This general difference in the behavior of the secondary wall has been correlated with the relative ease of preparation and the physical characteristics for conifer and hardwoods. Hemicellulose is distributed throughout the structure and has been related as the cementing substance in the cell wall.(3) Finally, the lumen, "composed mainly of proteinaceous materials," is quite narrow but provides an avenue of attack for water molecules.(5)

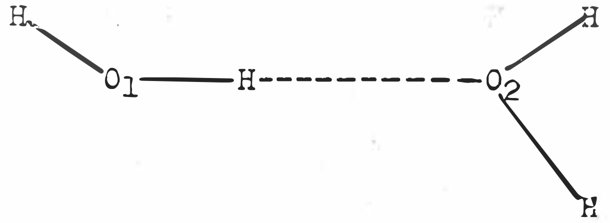
As mentioned previously, hydrogen bonding is important not only in the crystalline regions where the many bonds make the region relatively inert; but also is important in the amorphous regions where hydrogen bonds are attacked and broken by water vapor molecules. And as these bonds are broken, the fiber begins to swell allowing for exposure to more active surfaces. Thus it is important that the principles behind the complicated hydrogen bond be at least slightly understood.

Briefly, a hydrogen bond exsists between a functional group A-H and an atom or group of atoms B in the same or different molecule when:

1. There is evidence of bond formation and therefore large molecular aggregates or restricting of a molecular configuration.
2. There is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A.(6)

A hydrogen bond, therefore, usually lies between two closely spaced electronegative atoms A and B, usually restricted to oxygen, florine, nitrogen, and chlorine. One of the primary justifications for the formation of hydrogen bonds is the electrostatic effect.

Figure 3



Hydrogen Bonding Between Two Water Molecules

For example, if we consider the interactions between these water molecules, there exsists an interaction between the dipole O_1-H and the dipole directed from O_2 in the direction of the lone pair of electrons pointing toward O_1. The dipole moment O_1-H becomes such that H caries a net plus charge, and as a result it will abstract the lone pair of electrons on O_2. As a final result, the two molecules in a sense polarize each other causing an attractive force. (7)

Because of the nature of this interaction, hydrogen bonding may occur within the molecule (intramolecular), or may associate with other molecules (intermolecular). A combination of both types of bonding has been suggested for certain types of cellulose. The intramolecular hydrogen bonding occurs between the hydroxyl group of one glucose residue and the ring oxygen of the next residue. Two sets of intermolecular hydrogen bonding connecting the end hydroxyls and the bridge oxygens of the adjacent parallel chains are the other suggested bond types. (5)

In gross terms, hygroexpansion of paper can be explained by focusing on the process of forming a sheet. As water is evaporated from the sheet, fibers laying on the surface are pulled inward by the surface tension of the evaporation of the water medium. As the sheet compacts, a resistance to thickness contraction induces a hydrostatic negative pressure within the water medium. As the fibers contract, the entire web acts as an aggregate of contracting forces. If fibers are allowed to slide over one another, the contraction of the individual fibers will result in small amounts of fiber deformation and distortion. If however adhesive forces between fibers are sufficient to hold strains of the fibers in position, the distortion of the individual fibers will be more permanent. Since fiber to fiber bonding acts as an adhesive force, the fibers will be fixed in the position to which they have been drawn.(3)

When a dried sheet is exposed to an increase in relative humidity, the individual fibers begin to swell, thus increasing areas for water vapor combination and further swelling. Also the dried in stress and strains of the fibers are relaxed allowing the fibers to straighten and push out. Both of these factors combine to increase the sheet dimensions, and thus result in hygroexpansion.(3)

In an attempt to understand hygroexpansivity, those conditions which do not have a significant effect upon dimension changes should first be enumerated. Lorey reported that fiber size had no effect on the dimensional stability of sheets dried without restraint(8).Coarse fibers did however result in greater expansion.

In this same work, Lorey found that freeness levels had no effect except at higher freeness levels where pulps are bulky and expansion greater. Fahey(9), however, found the freeness levels had little effect on dimensional stability when handsheets were restrained during drying. In contrast to both, George(10) found high freeness levels exhibited lower hygroexpansions. His explanation was that the lower density and less fiber-to-fiber bonding at the high freeness levels allowed internal sheet expansion and fiber realignment. The total effect was therefore not transmitted to the external sheet dimensions. Tongren(11) found basis weight had no effect on hygroexpansion. George and Lorey(10,8) gave evidence that fillers exhibited no effect upon dimensional stability. Finally, George(10) found calendering to have little or no effect.

In contrast to the small number of independent variables, dimensional stability has numerous dependent variables. Maynard and George(12,10) both agreed that increased beating resulting in higher densities and more fiber-to-fiber bonds increased hygroexpansion. Their explanation was that the changes in fiber dimensions and fiber rearrangements are transmitted more fully to the external sheet dimensions.

Weidner(13), in his investigation of fiber dimension changes, found that increased beating resulted in a lower change in fiber width with a change in relative humidity. This smaller change is attributed to a loosening of the internal fiber structure and a corresponding opening of voids for water penetration. Tarkow(14) however indicated that fiber swelling can not alone be a criterion for sheet expansion.

Page(15) revealed that fiber width changes are dependent upon the degree of refining and pulp type. Dried fibers regain only 70% of their original width upon rewetting. Increased beating resulted in lower width regains. With sulfite pulps, the lack of width regain was most pronounced; while sulfate pulps returned to 93% of their orginal dimensions irrespective of the degree of beating.

Concerning the pulp type and their variation in expansion, George(10) reported unbleached softwood sulfite pulps gave the greatest dimensional stability. Tongren(11) generally found unbleached pulps more dimensionally stable than purified pulps. He attributed the purified pulp's greater expansion to its more accessibility to water vapor. Lorey(8) substantiated this when he found sulfite pulp's dimensional changes to increase as pulp purity increased. He also reported that similar hardwoods and softwoods expanded to the same extent. Fahey(9) found pulp type to have little effect on dimensional stability of a sheet restrained during drying. However, he also found pulp type to have a large importance when sheets were dried without restraint. Weidner(13) indicated that the degree of cooking had an effect on fiber widths. Overcooked and overbleached sulfite fibers had larger widths at all humidities than normally cooked unbleached fibers. Tongren(11) suggested that dimensional changes are somewhat dependent upon the hemicellulose content. Brecht(16) stated that residual lignin decreases the magnitude of dimensional changes. He also found that mechanical pulps gave greater dimensional stability than chemical pulps.

Laroque(17) found that the moisture history affects the dimensional stability of paper. He reported the extension-contraction behavior of paper became more regular after paper was subjected to several sorption processes. Since some stresses in paper are permanently removed during sorption, Calkins(18) suggested that this would tend to make changes more regular.

Harrison(19), experimenting with esterification of paper, determined that hygroexpansivity of paper was a function of the number of free hydroxyl groups present in the paper. Decreased numbers of free hydroxyl groups present reduced the hygroexpansion.

Ivarson(20) found the expansivity of paper to be considerably reduced by inducing drying stresses. Small stresses of 1-5 kg/cm^2 were effective in reducing expansion. Brecht(16) found that large drying stresses eventually resulted in actual shrinkage of the sheet.

Bialkowsky and Probst(21) indicated that fiber orientation in paper influenced dimensional changes. At 15-50% relative humidity, the "machine and cross" direction changes in dimension were the same. At 50-95% relative humidity, the "cross" direction changes were seven times as great as the "machine" direction changes. Weidner(13) found the ratio of the change in fiber width to length to be the same order of magnitude as the ratio of the change in "cross" direction and "machine" direction.

Brecht(16) found the rate of dimensional changes most rapid during initial absorption periods. High basis weight and density reduced the rate of dimensional change. Calkins(19) reported that increased shrinkage during drying produced less dimensional stable papers.

Both George and Warner(10,22) found synthetic fibers substantially reduced hygroexpansion. George found a 5% addition of 9mu, 3/16" long glass fibers reduce dimensional changes by reducing the shrinkage during drying. Cohen(23) reported that formaldehyde introduced into paper in the vapor form reduced dimensional changes. Watson(24) investigated urea formaldehyde and phenolic resins impregnation of paper, and found both gave more dimensionally stable sheets. Morton(25) found that cyanoethylation of paper was an effective method of reducing hygroexpansion, but also found it to reduce the paper strength.

Experimental Design

The experimental work was designed to determine the effect of the hydrogen ion concentration of the sheet forming water upon the hydroexpansion of the final sheet. A broad range of pH was therefore chosen for the experimental work. At low pH, hydrogen ions are readily available; while at a high pH, hydrogen ions become scarce. For example, at a pH of 2.0, hydrogen ions are 10^6 times more plentiful than at a pH of 10.0.

For this project, a bleached softwood kraft pulp was beaten in a Valley beater following Tappi test method T 200 m-45. After beating for 140 minutes, the pulp reached a freeness level of 374 c.c.

Following Tappi test method T 205 m-58, twenty handsheets were made with varied pH and contact times. At a pH of 7.0, 6.1, 4.0, and 2.2, 6M hydrochloric acid was added to the sheet water containing the diluted fibers until obtaining the desired pH levels. Because of the colloidal effect that alum exhibits at lower pH levels, hydrochloric acid was used in the acid pH adjustment rather than the traditional alum. Thus, by using HCl, unwanted variables at lower pH levels were avoided. At the pH of 10.0, 6M sodium hydroxide solution was added in the same manner as HCl.

At all pH levels, the fiber contact time was varied from 30 seconds, to 1 minute, and to 6 minutes. However, the method of timing was in all cases constant. The solution, either HCl or NaOH, was added to the diluted fibers in the British sheetmold; and simultaneously a timer was started. Ten seconds before the required time had elapsed, stirring was terminated. At the required time, the release valve lever was dropped; and the sheet was formed.

After pressing and drying, the sheets were tested for hygroexpansivity in a Neenah expansimeter. Using departmental recommendations, strips 6"by 1" were cut for test specimens. Also, humidity cycles were; 44.9% to 22.9% R.H., 22.9% to 88.0% R.H., and 88.0% to 22.9% R.H. For a R.H. of 22.9%, a saturated solution of potassium acetate was used; while potassium carbonate and barium chloride respectively were used for 43.9% and 88.0% R.H. Because of employment and school complications, the test duration time was reduced to three hours: one hour to equilibrate, and two hours for further equilibration and dimensional stabilization. Finally, the density of all test sheets was also determined.

Table I

Hygroexpansion for Several pH and Contact Interval Conditions

(Per Cent)

$-\log_{10}(H_3O^+)$	Contact Time (Sec.)	Hygroexpansion 43.9% to 22.9% R.H. (%)	Hygroexpansion 22.9% to 88.0% R.H. (%)	Hygroexpansion 88.0% to 22.9% R.H. (%)
10.0	30	.13	.50	.97
10.0	30	.14	.54	.97
10.0	60	.15	.77	1.09
10.0	360	.14	.89	1.10
7.0	30	.13	.63	.93
7.0	30	.14	.68	1.02
7.0	60	.15	.88	1.16
7.0	360	.13	.61	.47
6.1	30	.12	.94	.87
6.1	30	.12	.73	1.03
6.1	60	.15	.72	1.06
6.1	360	.14	.70	1.09
4.0	30	.16	.77	1.12
4.0	30	.15	.79	1.09
4.0	60	.13	.63	1.00
4.0	360	.13	.49	.95
2.2	30	.16	.90	1.13
2.2	30	.13	.68	.99
2.2	60	.16	1.06	1.17
2.2	360	.16	.84	1.13

Table II

Hygroexpansion for Sheets of Various Sheet Density, pH, and Contact Time

(Per Cent)

$-\log_{10}(H_2O^+)$	Contact Time (Sec.)	Sheet Density (#/ft³)	Basis Weight (#/25x40-500)	Hygro-Expansion (%)
10.0	30	.316	11 48.5	.50
10.0	30	.336	12 48.8	.54
10.0	60	.304	15 49.5	.77
10.0	360	.301	16 50.0	,89
7.0	30	.331	18 53.2	.63
7.0	30	.316	13 49.4	.68
7.0	60	.315	14 49.4	.88
7.0	360	.325	17 51.8	.61
6.1	30	.324	2 42.7	.94
6.1	30	.304	1 42.4	.73
6.1	60	.307	3 43.6	.72
6.1	360	.317	4 45.0	.70
4.0	30	.309	8 48.3	.77
4.0	30	.318	5 47.6	.79
4.0	60	.317	10 48.4	.63
4.0	360	.315	3 43.6	.49
2.2	30	.314	10 49.0	.90
2.2	30	.316	7 48.2	.68
2.2	60	.310	9 48.4	1.06
2.2	360	.299	6 47.7	.84

Table III

Average Hygroexpansion for Several pH and Average Sheet Densities

(Per Cent)

$-\log_{10}(H_3O^+)$	Average Hygroexpansion 43.9% to 22.9% R.H. (%)	Average Hygroexpansion 22.9% to 88.0% R.H. (%)	Average Hygroexpansion 88.0% to 22.9% R.H. (%)	Average Sheet Density ($\#/ft^3$)
10.0	.14	.71	1.03	.314
7.0	.14	.70	1.04	.322
6.1	.13	.77	1.01	.313
4.0	.14	.67	1.04	.315
2.2	.17	.89	1.12	.310

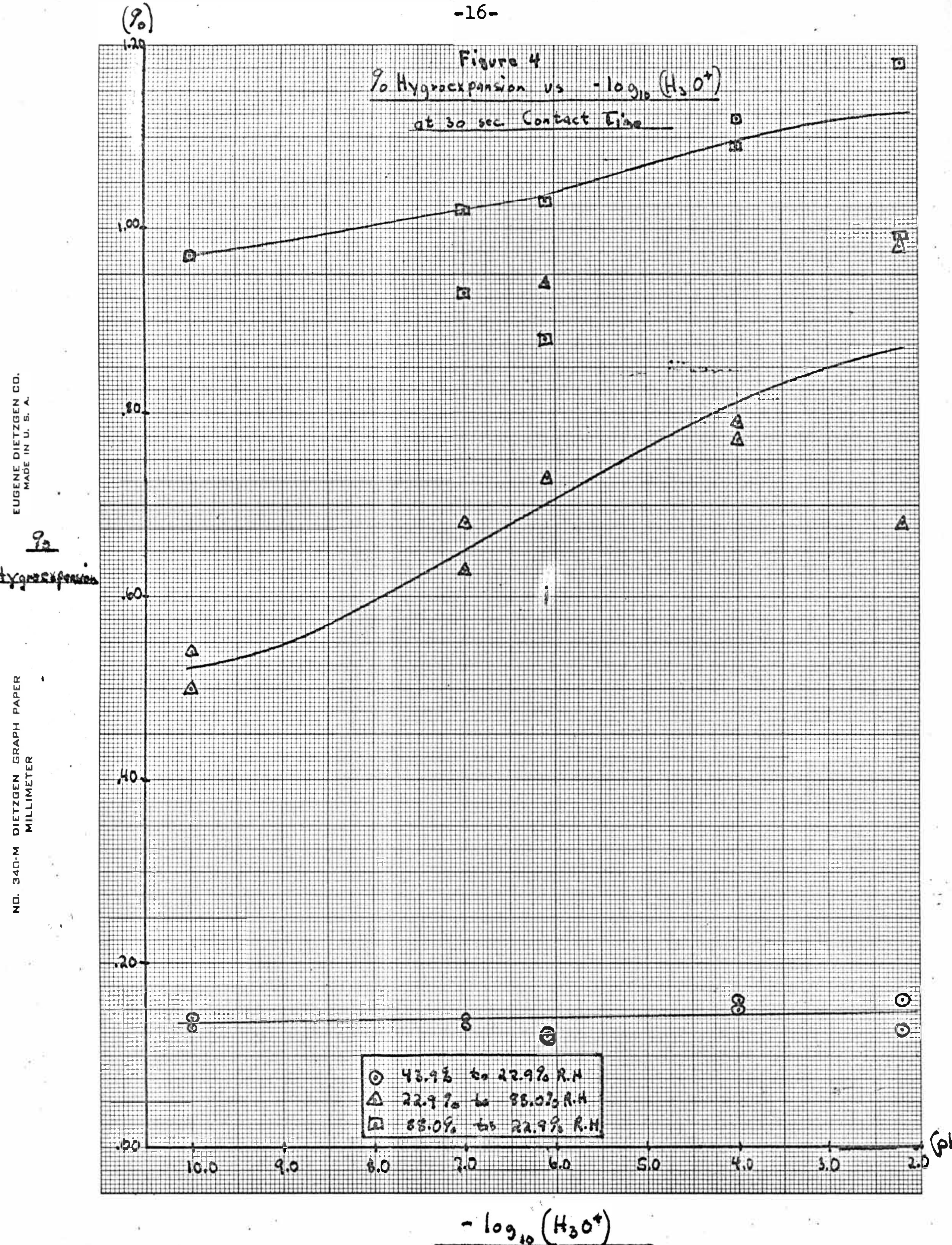
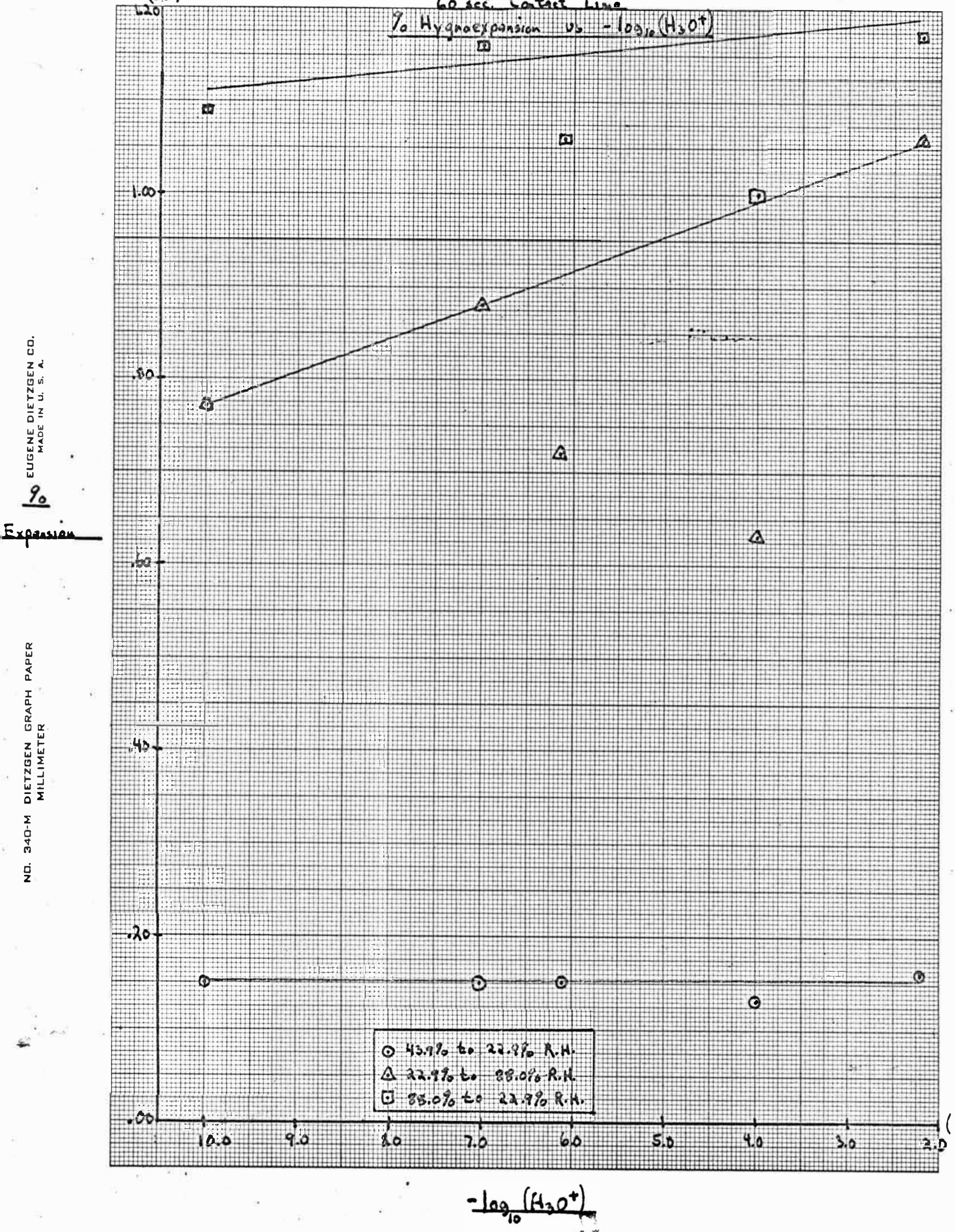


Figure 4

% Hygroexpansion vs $-\log_{10}(H_3O^+)$

at 30 sec Contact Time

Figure 5
60 sec. Contact Time



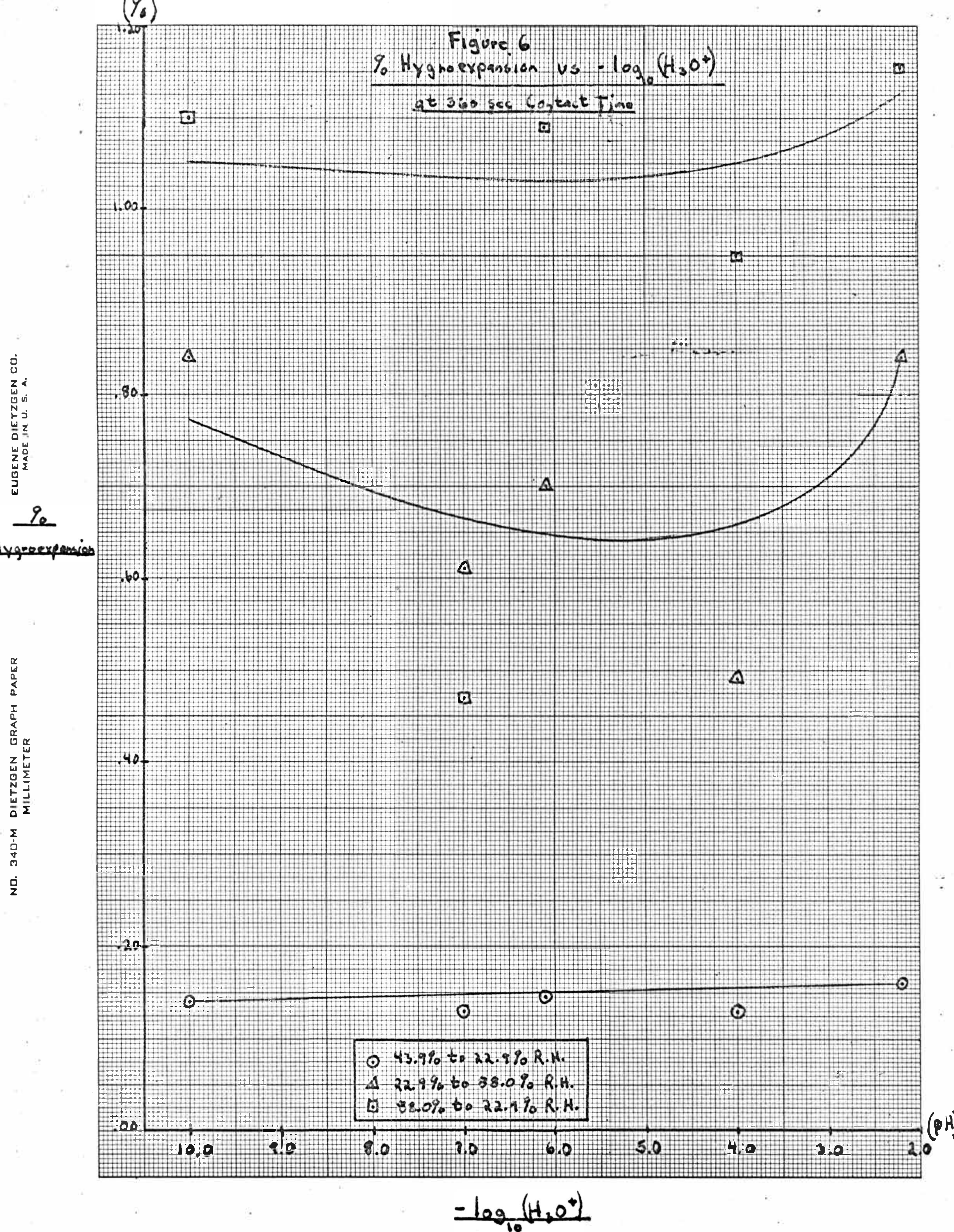


Figure 6

% Hygroexpansion vs $-\log_{10}(H_3O^+)$

at 360 sec Contact Time

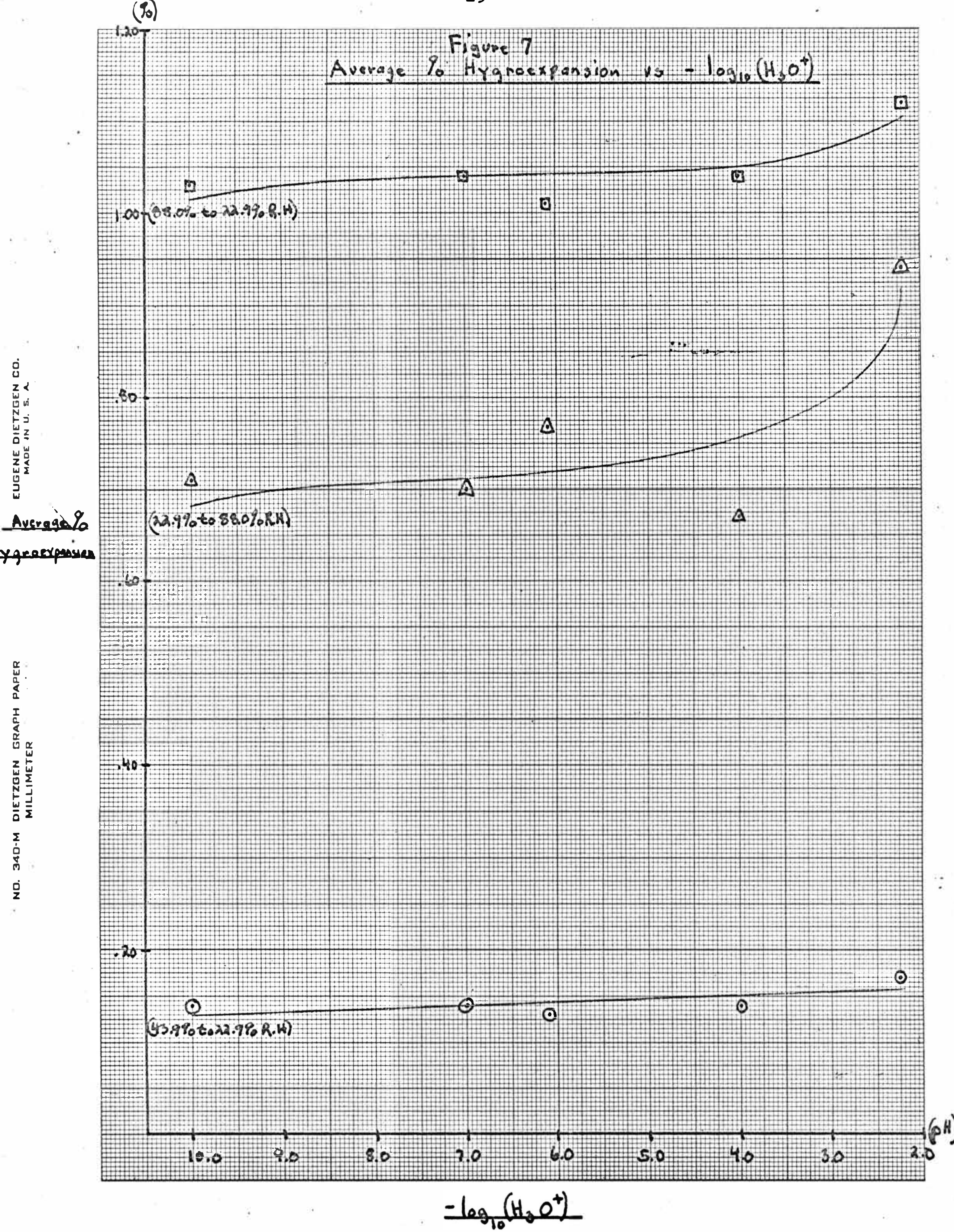


Figure 7

Average % Hygroexpansion vs $-\log_{10}(H_3O^+)$

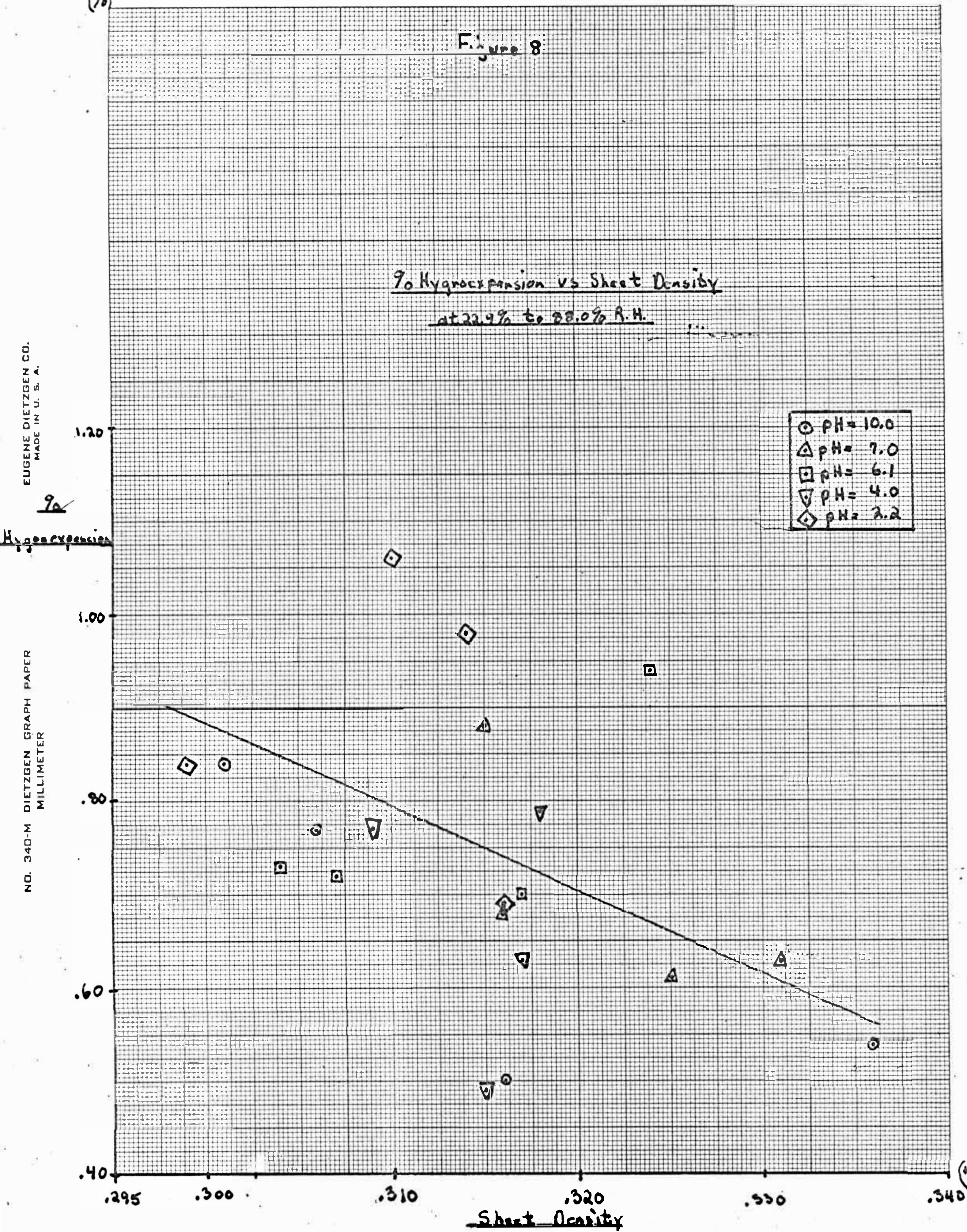


Figure 8

% Hygroexpansion vs Sheet Density
at 22.9% to 88.0% R.H.

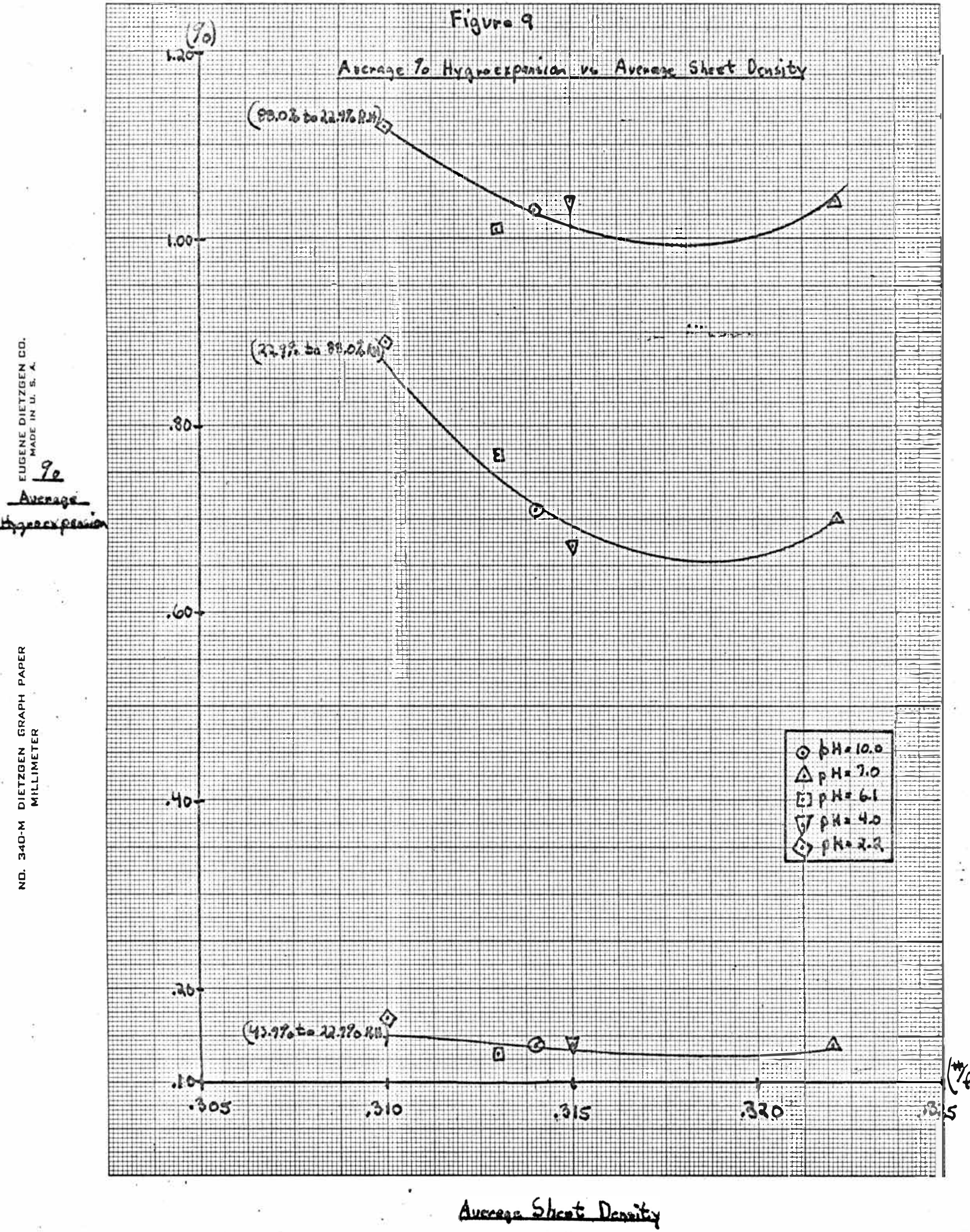


Figure 9

Average % Hygroexpansion vs Average Sheet Density

Discussion and Conclusions

From figures 4, 5, 6, and 7, it is evident that hygroexpansion increased slightly as the pH decreased. Considering the 43.9% to 22.9% R.H. cycle, the differences in hygroexpansion were very minor. With the 22.9% to 88.0% R.H. cycle, an increase in hygroexpansion with decreasing pH is very apparent. The 88.0% to 22.9% R.H. cycle, however, had a smaller increase in hygroexpansion with pH than the 22.9% to 88.0% R.H. cycle. In all cases, the contact time had little effect upon the degree of hygroexpansion or the general shape of the resulting plot of hygroexpansion and pH. Namely, the hygroexpansion at the 2.2 pH level was always greater than the hygroexpansion resulting from a pH of 10.0. Finally, the intermediate pH levels had well dispersed hygroexpansion values. In particular, on figure 7, the average hygroexpansion corresponding to a pH of 4.0 was in all cases below the average hygroexpansion corresponding to a pH of 10.0. Therefore, it must be concluded that there is no exact relationship between the degree of hygroexpansion and the pH level.

From figures 8 and 9, the sheet density is clearly the important factor influencing hygroexpansion. In figure 8, a decrease in the sheet density results in a distinct increase in hygroexpansion. Since the points are well dispersed, the pH evidently again has lettle effect on hygroexpansion. Figure 9 has a much clearer representation of this evidence. In the 22.9%

to 88.0% cycle, the two most dense sheets also have the lowest hygroexpansion. Conversely, the two most bulky sheets have the highest hygroexpansion. Since the order of hygroexpansion does not follow any pH relation, the pH must be concluded not to influence hygroexpansion. But rather, as is evident, the sheet density influences hygroexpansion. Since a more bulky sheet will allow faster equilibration, this sheet will have a higher initial hygroexpansion.as opposed to a dense sheet. Since the humidity cycles were terminated after only three hours, the bulky sheet, therefore, should result in higher hygroexpansion as was indicated in the experimental results.

In conclusion, this project indicates that there is no relationship between the pH level and the extent of hygroexpansion. This statement, however, holds true only if considering a test period of three hours. If the sheets were allowed to equilibrate more fully, a relationship between degree of hygroexpansion and the pH level may be found. This project, rather, found the sheet density to be the most important factor in the determination of initial hygroexpansion. After three hours of equilibration, the sheets with the lowest densities were also found generally to have the greatest dimensional instability; while sheets with high densities conversely had the greatest dimensional stability.

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