MOLECULAR CHARACTERIZATION OF ALKYDS
BY TURBIDIMETRIC TITRATION

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ABSTRACT

The primary factor influencing the viscosity of a traffic paint meeting Texas Highway Department specifications is alkyd resin characteristics. Experience has shown that reduced viscosities' characteristics of the resin do not always correlate with viscosities of the finished paint.

A turbidity titration method similar to the method used by Ivanfi and Ady[12] to determine polymer fraction distribution of resins was used to establish a distribution index for 55 alkyds previously used for the production of traffic paint. A study of the relationship between a resin's distribution index and the viscosity of fast dry traffic paint shows that turbidimetric titration will provide useful and practical data that can be used to predict viscosity characteristics of paint made from the alkyd resin.

Investigation of the infrared spectra of 16 alkyds selected from the alkyds used in the turbidity titration investigation showed the distribution index of a resin to be directly related to the absorbance ratio, $\frac{A_{ch}}{A_{ch} + A_{oh}}$, obtained from each alkyd spectrum. Since the absorbance ratio is indicative of the degree of polymerization of an alkyd resin, it is logical to assume that the distribution index of a resin is related to the structure of the polymers comprising the resin.

The relationship between the distribution index of a resin and the resin's polymer characteristics was confirmed by the results of gel permeation

chromatographic analysis of 19 of the alkyd resins. A plot of molecular weight of the precipitated polymer versus distribution index shows an excellent straight-line correlation.

The data from the gel permeation chromatographic analyses also reveals that the balance of high molecular weight fractions to low molecular weight fractions of alkyd resins are critical factors in the compatibility relationship existing between alkyd resins and chlorinated rubber.

Changes in alkyd specifications that will reduce production of traffic paints with abnormal viscosity variations and test methods to permit enforcement of these specification changes are proposed.

I. PURPOSE

By combining field experience as reported by District personnel with research in the laboratory, the Texas Highway Department has developed specifications for traffic paints and for raw materials used in traffic paints that provide for paints of insured quality with respect to appearance, performance and durability. However, limited ability to use raw material characteristics as a basis for predicting characteristics of the finished paint has discouraged some raw material suppliers and some paint manufacturers from bidding. Abnormal variations in paint viscosities with changes in sources of alkyd resin have been the primary source of concern.

In this study, attention is devoted to the alkyd resin, since this component was found to be the primary factor influencing viscosity variations of traffic paint meeting Texas Highway Department specifications. Although current specifications for alkyd resin solution provide the necessary information regarding chemical composition, physical properties determined by reduced viscosity measurements in the alkyd specification do not adequately characterize the alkyd polymer, nor do they always correlate with viscosities observed in traffic paints. Texas Highway Department specifications try to control an alkyd resin's contribution to a paint's viscosity characteristics by setting limits for the alkyd's reduced viscosity. This method has produced only limited success. Thus, it is the intent of this study to investigate and to provide explanations for the cause of abnormal viscosities in traffic paints, and to develop a method of analysis that will permit use of data describing certain physical characteristics of alkyd resins in the prediction of viscosities of traffic paint. If such predictions could be made prior to production, delays in production caused by alkyd resins with abnormal physical properties could be eliminated. In addition, the method would permit the establishment and enforcement of narrower viscosity ranges in traffic paints.

II. CONCLUSION

Results of this study show that the information concerning polymer properties obtained by the turbidity titration method is a valid means of predicting abnormal viscosities observed in traffic paints. The principles employed in the turbidimetric titration method have been adapted for use in proposed test procedure for traffic alkyd resins. The test procedure will permit the prediction of abnormal traffic paint viscosity by characterizing the alkyd polymer and will aid in the prevention of delays in traffic paint production caused by alkyd resins having undesirable physical characteristics.

III. RECOMMENDATIONS AND IMPLEMENTATION

It is recommended that the proposed test method be developed into a permanent test procedure to be included in the Texas Highway Department Paint Specifications. Implementation will proceed following consultation with alkyd manufacturers and paint manufacturers concerned with the production of traffic paint.

IV. DISCUSSION

The most baffling problem has arisen from those alkyds which met Texas Highway Department specifications, yet did not produce traffic paint within the specified viscosity limits. The advent of the alkyd resin - chlorinated rubber compatibility test resulted in eliminating alkyds known to produce "kick-out" problems with fast dry traffic paints. Nevertheless, abnormal viscosities in traffic paints are still occasionally encountered.

The problem of abnormal viscosities has been related to unusual physical properties of the respective alkyd resins. Physical properties of alkyd resins are governed by two important aspects, formulation and production techniques. Raw materials suitable for alkyd formulation are quite numerous. Cost plays a key role in any formulation in industry, and alkyd production is no exception. The three main components of traffic alkyd consist of a dibasic aromatic acid, conjugated oil or oil acids, and a polyalcohol.

Since the dibasic aromatic acid is specified in the Texas specifications to be ortho-phthalic acid or its anhydride, there is little room for substitution for this component in Texas traffic alkyd, although very small percentages of maleic anhydride are known to be used and, being highly reactive, it shortens the cooking time and makes the resin more viscous, harder and less soluble. The second component, oil or oil acids, is also restricted to soya or linseed oils, since these are the only two oils which currently meet requirements on refractive index and iodine number. A substitute recently being promoted for use in traffic alkyd resin is tall oil; however, a complete investigation into the possible effects that the rosin component of this material might impart to the completed paint has not been made to date.

The third component is the polyalcohols. This group offers a great deal of compounds to substitute into the alkyd formula and can produce large variations in the molecular structure of the finished alkyd. Glycerol, ethylene glycol, pentaerythritol, trimethylolpropane, and trimethylolethane are but a few of the most common polyalcohols available for use in alkyd production.

There are as many varieties of alkyd resins possible as there are blends that can be made from these three classes of constituents. The availability of T. C. Patton's[1] "alkyd constant" encourages a resin chemist to vary his formulation in order to use the most economical combination of materials.

Through use of the "alkyd constant", the chemist is able to predict many of the physical characteristics of an alkyd that will be produced from any combination of materials. In addition to characteristic variations resulting from changes in chemical composition, the type of equipment and production techniques used during manufacture significantly affect the molecular structure and physical properties of alkyd resins.

Two main processes are commonly used among alkyd manufacturers, the "solvent-cook" method and the "fusion-cook" method. The "solvent-cook" method generally produces alkyds of lower molecular size compared to the "fusion-cook" method. Differences in reaction time, kettle size, temperature and addition order of reactants also contribute to diverse properties obtained from different manufacturers.

The problem of determining certain physical properties of alkyd resins and the resins' effect on traffic paint viscosities thus becomes quite complex. An investigation of a given alkyd resin to determine adverse physical properties would require a complete quantitative and qualitative analysis of <u>all</u> components comprising the alkyd polymer, as well as taking into account the manufacturing process and techniques used. Such analyses would require an excessive amount of time and expense for routine tests. However, many of the physical properties can be described in terms of polymer fractions composed of molecular weight intervals obtained by a turbidimetric titration method.

According to Flory,

> "Characteristic features of the molecular weight distribution may be determined by turbidimetric titration of a very dilute solution of the polymer. A precipitant is added slowly to the agitated solution at constant temperature, and the turbidity due to precipitated polymer is measured by recording the decrease in the intensity of transmitted beam of light."[2]

The significance of such a titration has been discussed by several authors;[3,4,5] however, more recently, turbidity titration has found new applications in the coating industry in addition to gel permeation chromatography[6,7,8] and related molecular weight parameter determinations.[9,10,11] The titration method outlined by Ivanfi and Ady[12] provides a rapid determination of fraction distribution for alkyd resins. The apparatus and materials required for such a determination are described fully in the article by Ivanfi. In this study the method was revised to accommodate use of the ultraviolet visible spectrophotometer, due to its availability in this laboratory. Additional apparatus required includes a 100 ml buret, magnetic stirrer, 500 ml conical flask, and a 200 ml volumetric flask.

A fundamental description of the procedure for a routine determination of a distribution curve is as follows:

A weighed sample of alkyd resin solution containing approximately one gram of solid alkyd resin is dissolved in 200.0 ml (measured by volumetric flask) of methyl isobutyl ketone in a 500 ml conical flask, and the solution is stirred by magnetic stirrer until uniform concentration of the resin is achieved. The solution should be maintained at a temperature of 25°C throughout the titration. Approximately 3 ml of the solution is extracted and placed in a standardized 1.0 cm quartz cuvette and the cell is mounted in position in the ultraviolet visible spectrophotometer. Specific setting for the parameters of the spectrophotometer appear in Table I.

The wavelength selected was in the visible range of the electromagnetic spectrum. The reason for using this particular wavelength (λ - 750 mμ) was to minimize absorbance variations with changes in volume fractions of the solvents used in this method. Flory[13] and Billmeyer[14] also note that for light-scattering methods, when the dimension of the precipitated particle (in Angstroms) exceeds λ /20 (λ = wavelength expressed in Angstrom units), the angular dependence of the intensity of the scattered light deviates appreciably from the equation relating scattered light intensity to molecular weight.

The value λ /20 was considered to be a suitable criteria for the 750 mμ wavelength selection in the turbidimetric titration method, based on estimated values of chain length obtained from the work on short oil alkyds by Rybicka, Olley and Cronin.[15]

Other parameters given in Table I were selected to obtain optimum efficiency from the spectrophotometer. Upon placing the sample in position in the spectrophotometer, the instrument is standardized at 0% Transmittance with the sample shutter closed and 100% Transmittance with the sample shutter completely opened. Once standardization is completed, the sample is removed from the cuvette and replaced in the flask. The cuvette is then washed thoroughly and dried. The flask is replaced on the magnetic stirrer and the polymer solution is titrated with methyl alcohol under continuous stirring.

The rate of addition of methyl alcohol should be adjusted so that developing turbidity occurs only briefly in the vortex produced by the stirring bar. The concentration of methyl alcohol should not be allowed to accumulate in an isolated area of the flask. This can be avoided by judiciously adjusting the rate of agitation and rate of methyl alcohol addition from the buret.

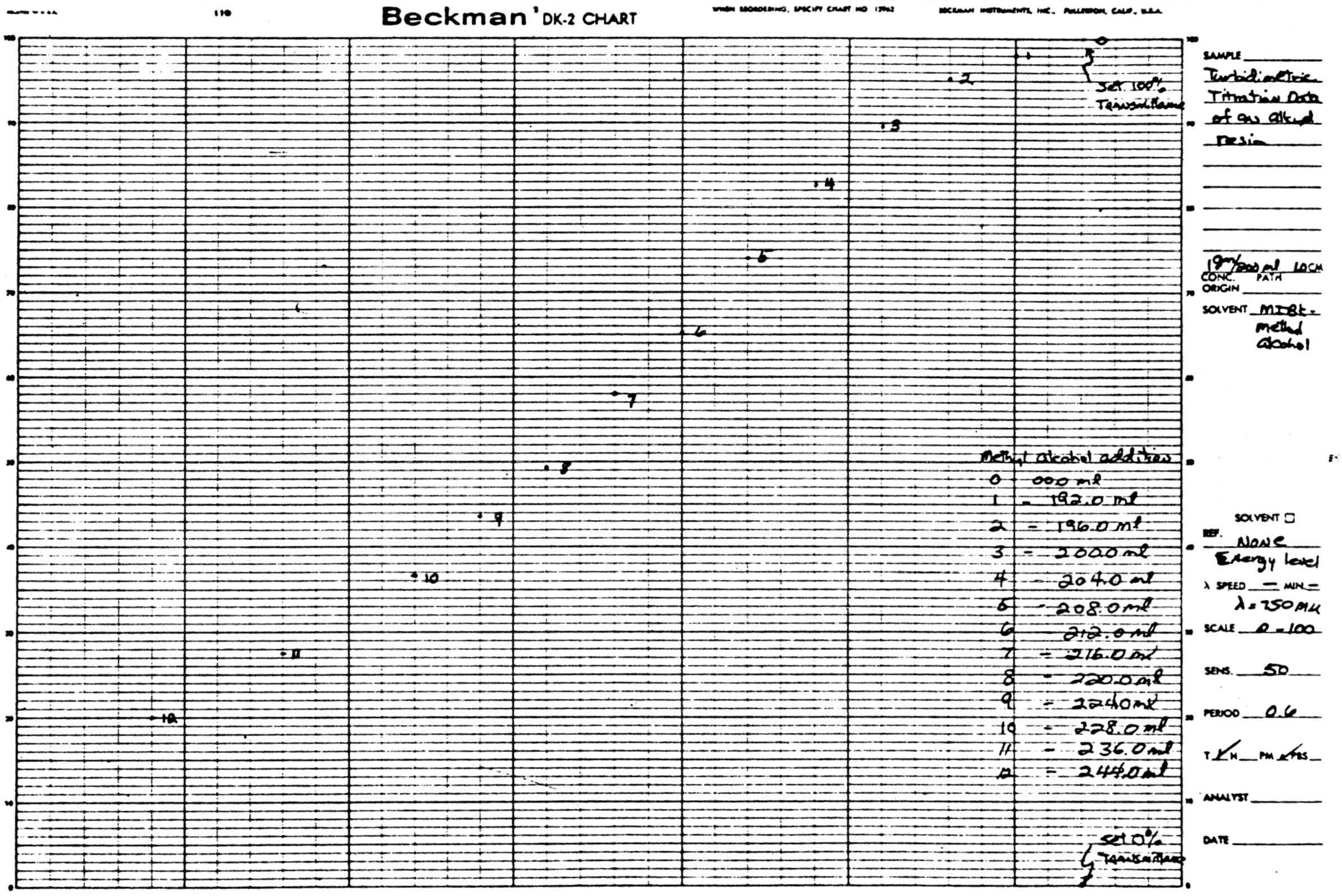
The amount of methyl alcohol required for polymer precipitation is dependent upon the molecular size or molecular weight range of the polymer in question.

> "The turbidity increases faster, the higher the molecular weight of the preparation or the higher the portion of the largest molecules of the preparation. At the beginning of the titration, the more rapidly the turbidity increases, the greater the proportion of these molecules in the tested polymer.

> "In the solution of polymers characterized by a narrow range of molecular weight distribution, a hardly perceptible turbidity occurs at first, when the precipitating agent is added. Above a certain level of precipitating agent, however, a rapidly increasing turbidity may be observed. In polymers, including portions with a much higher average molecular weight, turbidity occurs substantially sooner and increases evenly."[16]

For the traffic alkyds investigated in this study, a range of 130 ml to 445 ml of methyl alcohol was found to be the limits of precipitating agent addition necessary to characterize the sample. Titration is continued to the first visible turbidity, at which point a 3 - 4 ml sample is extracted from the flask and delivered into the standardized 1.0 cm quartz cuvette. The % Transmittance is measured on the ultraviolet visible spectrophotometer and corresponding volume of methyl alcohol is recorded. The sample is returned to the flask and the titration is continued. It was found that, in general, the most critical measurements are those taken between 80% and 20% Transmittance. The average number of readings taken for a given sample is 10. The more readings taken, the more precise the resulting distribution curve. Most samples require transmittance measurements every 2 - 4 ml increments of methyl alcohol addition. An example of the data obtained appears in Figure 1.

The significance of the information obtained does not become apparent until mathematical operations are applied to the data. A normalization procedure which minimizes error is of primary importance in interpreting the data.



SAMPLE Turbidimetric Titration Data of an alkyd Resin

1gm/200 ml 1.0CM
CONC. PATH
ORIGIN
SOLVENT MIBK-methyl alcohol

Methyl alcohol additions
0 - 000 ml
1 - 192.0 ml
2 - 196.0 ml
3 - 200.0 ml
4 - 204.0 ml
5 - 208.0 ml
6 - 212.0 ml
7 - 216.0 ml
8 - 220.0 ml
9 - 224.0 ml
10 - 228.0 ml
11 - 236.0 ml
12 - 244.0 ml

SOLVENT ☐
REF. NONE
Energy level
λ SPEED — MIN. —
λ = 250 mμ
SCALE 0 - 100
SENS. 50
PERIOD 0.6
T ✓ H PM ✓ PRS
ANALYST
DATE

Figure 1

Turbidimetric Titration
Raw Data

Ivanfi and Ady utilize the Tung exponential function to "eliminate inaccuracy due to the scatter of measurement results".[17] Definitions of terms used in the exponential function are as follows:

V = volume fraction of precipitating agent methyl alcohol (experimentally obtained value)

T = % Transmittance

Z = turbidity value

= 1 - % Transmittance

I_V = function of V

= $1 - Z$ as defined by Ivanfi and Ady

= $1 - (1 - T) = T$

The Tung exponential function is expressed by the following relationship:

Equation 1

$$\log \left[\log \frac{1}{1 - I_V} \quad / \log e \right] = \log a + b \left[\log \frac{1}{V} \right]$$

where "a" and "b" are defined as the distribution parameters. Since experimental values I_V and V are known, a plot of $\log \left[\log \frac{1}{1 - I_V} \quad / \log e \right]$ as the ordinate versus $\log \frac{1}{V}$ yields an approximate straight line whose slope is "b" and whose "y" intercept is log "a". The values "a" and "b" are derived from the straight-line plots for data between approximately 20% - 80% turbidity.

Upon determining the distribution parameters "a" and "b" for a given sample, the differential curves can be calculated. The mechanics of the mathematics applied in the method are derived from a differentiation of the Tung exponential function (Equation 1).

The differentiated form of the integral equation appears as:

Equation 2

$$\frac{d^{I_V}}{d_V} = \frac{a \cdot b(\frac{1}{V})^{b - 1}}{e^{a(\frac{1}{V})^b}}$$

By substituting the calculated parameters "a" and "b", and the experimentally obtained values for V, the values for $\frac{d^{I_V}}{d_V}$ are calculated for each volume increment recorded in the titration. The resulting data for $\frac{d^{I_V}}{d_V}$ are then plotted on the ordinate scale versus $\frac{1}{V}$ on the abscissa scale. Such a graph yields the differential distribution curve characteristics for a given sample. An example of calculations involved for a titration appears in the Appendix (see Sample Calculation, pages 35 - 40.) Titration data and calculated values for samples investigated in this study appear in the Appendix, Table II. The peak maximum for each differential distribution curve was identified by the corresponding reciprocal volume fraction of methyl alcohol $(\frac{1}{V})$ on the abscissa of each distribution curve. This value $(\frac{1}{V})$, termed the distribution index, was used to characterize each sample and to correlate each sample with molecular weight and molecular size distribution characteristics, infrared spectra and viscosity of traffic paint.

The turbidimetric titration method was applied specifically to traffic alkyd resins used in production of traffic paints. Fifty-five samples, representing six major producers of alkyd resins, were investigated according to their differential distribution curves. The peak height of the distribution curves was recorded according to the distribution index, reciprocal volume fraction obtained for each sample. Of the 55 samples investigated, 42 samples were used in actual production of fast dry traffic paint by five major paint manufacturers. Correlation of the actual viscosities observed in traffic paint production with the distribution index $(\frac{1}{V})$ was the first relationship revealed.

The 42 alkyd resin samples taken during production of traffic paint were recorded according to their distribution index and physical properties observed in the respective batches of traffic paint (Appendix, Table III). Upon plotting the distribution index of a given sample and the observed viscosity (in KU's) of the given traffic paint formula, a nearly straight-line correlation was found to exist. This relationship was found to be a usable criteria for predicting viscosities of a finished paint prior to production. Since WPT-8, white traffic paint and YPT-8, yellow traffic paint are big volume items in Texas, an attempt to correlate alkyd characteristics with paint viscosity for these two systems was made. The distribution index versus viscosity in KU's is plotted for these two systems (Appendix, Graphs 1 & 2). Paints used to provide data for Graphs 1 and 2 had gallon weights within ± 0.05 lbs. of the theoretical gallon weight. It may be noted that the WPT-8 curve exhibits a steeper slope than does that of YPT-8, indicating that the yellow fast dry traffic paint is more sensitive (viscosity-wise) to alkyd polymer distributions than is the WPT-8, white traffic paint. In addition, the curves at either end of the viscosity ranges of both paints become somewhat vague in correlation. This may be attributed to increased effects of oil absorption properties of the pigments and extenders used and to the varied manufacturing processes utilized during production. Therefore, as the predicted viscosity approaches 67 - 68 KU's the method by turbidimetric titration becomes less reliable. Similarly, distribution factors for alkyds which indicate viscosities in excess of 90 KU's also become less reliable in predicting the actual viscosity of the paint due to the same factors, oil absorption and manufacturing procedure. Alkyds producing high viscosities pose greater problems concerning compatibility and often produce paint with much higher viscosities than anticipated. Nonetheless, samples within the 68 - 90 KU's range were found to follow the correlation with distribution index with very few exceptions.

Application to modified traffic paint formulas was also investigated. These paints were formulated by varying the chlorinated rubber to alkyd ratio, as compared to the present YPT-8b formula. Viscosity correlations with the distribution indices of selected alkyd resins were plotted for three modified traffic paint formulas (see Appendix, Table IV). All samples of these modified formulas were made in identical fashion so as to minimize differences in grinding technique, solvent evaporation, etc. Results of the viscosity correlations obtained are shown in Graph 3. It is interesting to note the noticeable effect of chlorinated rubber (20 cps) on the viscosity range of the paints made in this study, i.e., the greater the percentage of chlorinated rubber, the higher is the viscosity of the paint. However, the pattern of paint viscosity dependence upon D_i for each alkyd still yields the relationship necessary to characterize the viscosity range for the given traffic paint formulas.

Efforts to characterize alkyds according to composition revealed by infrared spectrophotometry have revealed some correlation with distribution curves obtained with the titration technique. The first trend observed became apparent upon examining the infrared spectra of 16 alkyds (Appendix, Graphs 4a-4p) whose distribution curves had been plotted. A comparison of the absorbance of the hydroxyl stretch (O-H stretch) in alkyd spectra with the distribution index shows this trend. Specifically, the lower the distribution index, the higher is the absorbance value for the O-H stretch, also, the higher the distribution index, the lower is the absorbance of the O-H stretch. The relationship was found to be the ratio of the C-H absorbance (2960 cm^{-1}) to the sum of the absorbances of the O-H (3540 cm^{-1}) and C-H (2960 cm^{-1}) stretches.

The procedure used to obtain infrared curves of alkyd resin samples is as follows:

Alkyd resin solution (60% in VM&P Naphtha) sufficient to give 1.1 - 1.2 grams of solid resin is weighed in a tared cup, put in solution with perchloroethylene (spectrophotometric grade), and diluted to volume in a 50 cc volumetric flask. A demountable KBR cell with .200 mm shim was used in obtaining the infrared spectra of the alkyd samples. Results of the study show a straight-line relationship exists between the absorbance ratio and the distribution index obtained for each respective sample (Graph 5). Data for the absorbance ratio and distribution index appears in Table V.

The absorbance of the O-H stretch observed in the infrared spectra of alkyds is "usually attributed to the O-H of the polyhydric alcohol, which is generally present."[18]

The characteristics of the various polyalcohols used in alkyd formulation will affect the absorbance of the O-H band of an alkyd spectrum. This has been demonstrated by the effect of hydroxyl number on alkyd resin where,

> "Infrared spectrophotometric curves were run on five alkyds of varying hydroxyl numbers. No differences in the curves were seen other than the absorption in the hydroxyl area of the band. This absorption was proportionate to the hydroxyl number as determined by chemical analysis."[19]

(Note: These five alkyds were designed with minimum structural and molecular weight differences.)

It may be noted that most traffic alkyds utilized by the Texas Highway Department contained glycerol or a predominance of glycerol as the polyalcohol. Verification by chemical analysis of phthalic anhydride as the dibasic acid and soya or linseed oil as the oil components of alkyds used in our study, puts all alkyd samples investigated in the same category of basic composition; glycerol, phthalic anhydride, soya or linseed oil type alkyds.

Based upon the infrared data obtained in our study, it is proposed that in alkyds of similar composition, differences observed in hydroxyl band absorbances relative to carbon hydrogen stretches of alkyd infrared spectra can be attributed to free or unreacted polyalcohol, and thus is a measure of the degree of polymerization. Such a proposal explains the types of correlation existing between the distribution index and the O-H absorbance relative to the C-H absorbance.

Having observed the correlation existing between infrared spectra of alkyds and their distribution indices, and encouraged by the statement,

> "According to investigations of Schulz,[16] the precipitating agent concentration V_i at the beginning of the i-th polymer, is about inversely proportional to the molecular weight, if V stands for the precipitating agent concentration, expressed as percentage of the weighed polymer solution. Therefore, in principle, data obtained by turbidity titration are suitable to plot curves characterizing the molecular weight distribution."[20]

the gel permeation chromatographic analyses were initiated to investigate molecular weight and molecular size distribution characteristics of selected samples used in the turbidimetric titration method.

Gel permeation chromatography (G.P.C.) is basically a method for separating polymer molecules according to size. The results of a G.P.C. analysis yield a molecular size distribution which can be related by calibration to molecular weight distribution. Certain concepts of G.P.C. require defining before one can grasp a meaningful understanding of the information obtained. Elution volume of the sample solution, measured in 5 cc increments, is the key to the relationship with molecular size and molecular weight. Since high molecular size fractions of a polymer are first to be eluted from the columns, it follows that the lower the elution count, the higher the molecular size, and vice versa. The values assigned to molecular size are based on the calibration standard. Polystyrene and polyglycol standards were selected as the calibration standards for the G.P.C. analyses conducted in this study. Nine standards of known molecular weight and molecular size were used to calibrate the elution counts for the set of conditions used in this analysis. (See Calibration Data, Appendix, Table VI.) Thus, alkyd fractions eluting at particular elution counts were assigned molecular weight corresponding to the calibration curve established by polystyrene and polyglycol standards.

The molecular weight obtained for the alkyd fractions is related to molecular size by the "Q" factor by the following equation:

$$\frac{\overline{M}_w}{Q} = \overline{A}_w$$

where

$\overline{M}_w$ = molecular weight

$\overline{A}_w$ = chain length in Angstrom units

Q = Q factor

for polystyrene Q = 41

for polyglycol Q = 16

The following discussion of G.P.C. analysis, results and its relationship to the distribution index will mention both molecular weight and molecular size. Therefore, it should be remembered that these two terms are related by a constant factor relative to the calibration standards.

Difficulty is exhibited in obtaining an accurate molecular weight distribution of an alkyd resin when the G.P.C. is calibrated with a totally different type of polymer. Thus, molecular chain lengths and molecular weights obtained in this study are only relative and not absolute, since polystyrene and polyglycol standards were used to calibrate the G.P.C. prior to analysis of alkyd resins. Recently, Rybicka, Olly and Cronin[21] instituted G.P.C. analysis of alkyd compositions during alkyd synthesis. Their molecular weights and chain lengths are to be considered far more reliable, since the G.P.C. was calibrated by vapor pressure osmometry number averages of alkyd samples. Nevertheless, this study was considered to be very useful for molecular weight distribution characteristics, as the polystyrene calibration was used throughout the analyses providing a consistent basis for comparative analysis.

Nineteen alkyd resin samples representing six producers were selected for G.P.C. analysis by the Department of Physics, Texas A & M University. The instrument, a Waters Associates Model 200 G.P.C., was equipped with $50/10^2/10^3/10^4$ Å columns operating at an ambient temperature of 25.0°C. Tetrahydrofuran was the selected carrier solvent. The first group of

10 samples submitted for G.P.C. analysis was returned with the corresponding chromatograms appearing in Appendix, Graph 6a-6j. Sample analyses of this first group of alkyd resin samples exhibited excellent differences in samples over the range of low to high molecular weight ranges. Consultation with Texas A & M personnel resulted in a change of columns to be used in the second set of samples submitted. Column sizes were changed to $10^3/10^4/10^5/10^6$ Å, with the rest of the operating conditions remaining the same. The chromatograms of the second group of samples appear in the Appendix, Graphs 7a-7i. The chromatograms of the second group do not exhibit the noticeably high weight fraction peak observed in the first set of samples. Sample 55 provided the basis for comparing the two sets of operating conditions.

Molecular weight averages were computed for each sample chromatogram by the conventional method:

$$\bar{M}_w = \frac{H_i \; M_i}{H_i}$$

where

$\bar{M}_w$ = molecular weight average

H_i = height of chromatogram

M_i = molecular weight based on polystyrene

Results of $\bar{M}_w$, molecular weight average, versus distribution index exhibited a trend, but no positive correlation. Relationships were observed to exist between the distribution index and the percent polymer (from G.P.C.) being above a given molecular weight. The percent polymer was computed from data obtained from cumulative plots of the gel permeation chromatograms, Table VII. The molecular weight chosen proved to be critical in obtaining a positive correlation. Recording the percent polymer being above 12,000 molecular weight units versus distribution index (Appendix, Graph 8) for the sample yielded an exponential curve. A significantly large portion of samples were found to be quite close to the equation fitting this curve.

Hillyer and Leonard conducted a study on the reduced viscosity of short oil alkyd resins. They formulated an equation which "consistently gave effective molecular weights which at a given concentration corresponded well with the observed shifts in viscosity."[22]

The equation is:

$$M \text{ eff} = M \exp \left(\phi_1^{-\Sigma \gamma_1} - 1 \right)$$

where

M eff = the effective molecular weight

M = true molecular weight

ϕ_1 = volume fraction of solvent

Σ = a constant

γ_1 = the volume activity coefficient of the solvent

It may well be that the observed percent polymer $>$ molecular weight = 12,000 versus distribution index is an example of this relationship.

One other correlation obtained from the G.P.C. data was the comparison of the percent polymer precipitated in the turbidity titration with the distribution index.

With regard to the relationship of precipitated polymer in a turbidimetric titration to molecular weight, Flory states that,

> "An empirical correlation must first be established between the concentration of the precipitant and the molecular weight of the polymer precipitated at a specified polymer concentration. The experimental curve expressing turbidity as a function of the concentration can then be converted to an integral molecular weight distribution curve."[23]

Since no absolute measurement was available for determining the molecular weight of the polymer at a given point in the turbidimetric titration, the percent polymer precipitated at the volume fraction of methanol (corresponding to the distribution index) was assumed to be related to the molecular weight distribution obtained from the G.P.C. analyses.

Also, the percent polymer precipitated for each sample was made relative to the sample exhibiting the lowest distribution index, Sample 113. Thus, Sample 113 was arbitrarily assigned 100% polymer precipitated at the volume fraction of methanol corresponding to the distribution index. The percent polymer precipitated was expressed for all subsequent samples investigated by G.P.C. as:

$$\% \text{ polymer}_{ppt} = \frac{V_{D_i} \text{ (Sample X)}}{V_{D_i} \text{ (Sample 113)}}$$

where

$\% \text{ polymer}_{ppt}$ = percent polymer precipitated

V_{D_i} (Sample X) = volume of methanol corresponding to the distribution index of Sample X + 200 ml MIBK

V_{D_i} (Sample 113) = volume of methanol corresponding to the distribution index of Sample 113 + 200 ml MIBK

The distribution index (D_i) for Sample 113 is 1.45, which is the value of the reciprocal volume fraction (V_f) of methanol. Thus:

$$D_i = \frac{1}{V_f}$$

$$\frac{1}{1.45} = V_f$$

Taking into account that 200 ml of methyl isobutyl ketone composed the original alkyd solution, one can calculate the methanol solution corresponding to the distribution index as follows:

$$\frac{1}{1.45} = \frac{X \text{ ml}}{X \text{ ml} + 200}$$

where

X = ml of methanol added

= 444.44 ml

X + 200 = 644.44 ml = total volume of solution containing 1 gram of alkyd resin

The total solution volume for each sample was calculated and then normalized with respect to the total volume (644.44 ml) of Sample 113. The fraction obtained for each sample was then expressed as the percent polymer precipitated. The value obtained for the percent polymer precipitated (X%) was then used to determine the molecular weight at the point that X% polymer had eluted from the G.P.C. This was accomplished by multiplying the percent polymer precipitated by the total number of counts computed for the cumulative plot of each respective sample. The resulting number was then matched to the closest value of cumulative values and the corresponding molecular weight recorded.

Data compiled for computing the percent polymer precipitated appear in Appendix, Table VIII, along with the total counts of the cumulative distribution plots and the corresponding molecular weights. The plot of distribution index versus molecular weight of precipitated polymer is given in Graph 9.

The resulting graph (Appendix, Graph 9) of molecular weight obtained for the polymer precipitated versus distribution index shows an excellent straight-line correlation. By obtaining a distribution index for a given alkyd sample by the titration method, one can estimate the molecular weight of the polymer at that volume fraction of methyl alcohol.

The G.P.C. data provides clues to solving a specific problem encountered in fast dry traffic paint production - incompatibility with chlorinated rubber. The compatibility test employed in the traffic alkyd specification was established to screen alkyds which exhibited a phase separation with chlorinated rubber - methyl ethyl ketone solution. The cause of this phenomenon is still being investigated; however, recent related work being done in this field is directed at solving phase separation in binary solvent mixtures with a single polymer; short oil alkyd being the solute. It is assumed that the concept of molecular aggregation mentioned in Hillyer's et al paper might be applied to a binary polymer system as well; alkyd-chlorinated rubber. The problem of predicting phase separations may be explained by the complex compositions of alkyd resins. "In particular, the oil component may act as a suspending agent and, as such, have a stabilizing influence on the resin aggregated or clusters."[24]

With this concept in mind, an attempt was made to derive some relationship between alkyds producing an incompatibility with chlorinated rubber and the G.P.C. data obtained for each such sample.

It was assumed that the highest molecular weight fraction of an alkyd would most likely lead to the insoluble phase in the compatibility test. Based on Hillyer's statement,[24] the oil component of the alkyd would appear as one of the lowest fractions of the alkyd in the gel permeation chromatogram. Thus, the percent of the polymer being below a given elution count (molecular weight calibrated to polystyrene) could represent the high molecular weight fraction and the percent polymer being above a selected higher elution count could represent the low molecular weight fraction of the polymer. Figure 2 shows a chromatogram of an alkyd sample that was observed to produce an incompatible solution with chlorinated rubber and methyl ethyl ketone solution. Elution count #20 was selected as the lower boundary for the high molecular weight fraction of the alkyd sample, and elution count #26 was selected as the upper boundary for the low molecular weight fraction. Obtaining the percent polymer by dividing the sum of heights below count #20 by the total sum of the heights of the whole chromatogram, count #19-34, gives the percent polymer less than count #20, or greater than molecular weight 7,000. Similarly, the value for percent polymer above count #26 is calculated. This value corresponds to the percent polymer less than molecular weight 2,000. The percentages obtained yield the upper and lower molecular weight fractions of the polymer. Upon dividing the percent polymer less than count #20 by the percent polymer greater than count #26 gives a "compatibility index" which correlates with observed compatibility tests conducted on selected alkyds investigated in this study. The results appear in tabulated form in Table IX in the Appendix.

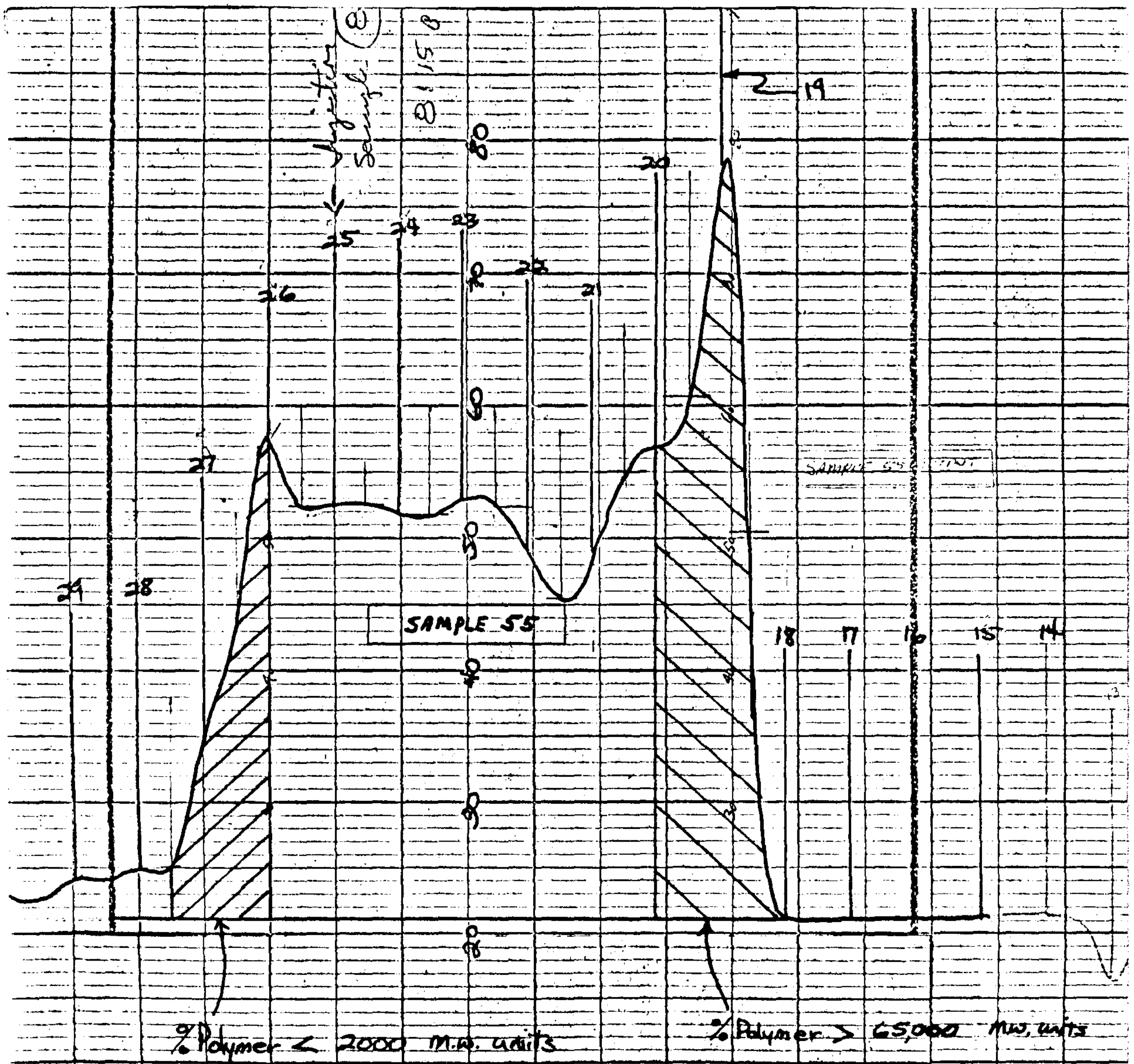


Figure 2

G.P.C. Data Illustrating Compatibility Index

Although this relationship is informative as to the possible cause of "incompatible" alkyds, it is not sufficient to explain every aspect of phase separation. This observation is empirical and does not explain possible physical or chemical interaction of alkyd with chlorinated rubber. It should be stated that all compatibility tests conducted on alkyds in this series were performed with the same solution of chlorinated rubber - MEK, so as to minimize differences in the chlorinated rubber polymer.

Unfortunately, the high and low molecular weight fractions are not revealed in a turbidimetric titration. Therefore, the current compatibility test is considered to be the best method available at this time for determining compatibility.

Relationships revealed by studies of infrared spectra and gel permeation chromatographic analyses substantiate the use of the distribution index to characterize the alkyd polymer. However, to apply the turbidity titration method of analysis to traffic alkyd samples on a routine basis would be involved and time-consuming. Therefore, a modification of the titration method has been made in order to produce a practical test procedure that will characterize the polymer properties of alkyds as related to traffic paint viscosities.

As specified by the Texas Highway Department, traffic paints having a viscosity in excess of 80 KU's and below 70 KU's are considered to be undesirable. Examination of the YPT-8 and WPT-8 viscosity dependence upon the distribution index (Appendix, Graphs 1 and 2), reveals that the upper limit of viscosity (80 KU's) corresponds to a distribution index value of 2.20. A solvent blend of 6 parts by volume of methyl isobutyl ketone to 5 parts by volume of methyl alcohol produces a solution with the equivalent value of D_i - 2.2. This solution (described as solvent $Di_{2.2}$) has been used to characterize selected alkyd resin samples by the following method:

A weight of alkyd resin solution sufficient to yield 0.4 - 0.6 grams of alkyd resin solids is weighed into a 250 ml wide-mouth Erlenmeyer flask and dissolved under agitation (by magnetic stirrer) with a given amount of solvent $Di_{2.2}$. The exact volume of solvent to be added to the alkyd sample is calculated by the following equation:

Equation 3

$$X = 200\ W_s$$

where

X = ml of solvent $Di_{2.2}$ to be added to the weighed sample

W_s = sample weight (grams) of alkyd resin solids as determined by Federal Test Method Standard No. 141a, Method 5071 or 5072.

The alkyd sample and solvent $Di_{2.2}$ are agitated by magnetic stirrer until uniform concentration of the polymer is achieved. The ultraviolet visible spectrophotometer is operated under the same conditions used in the turbidity titration method (Appendix, Table I). The instrument is standardized by setting the pen to record 0% Transmittance with the sample shutter closed, and the 100% Transmittance is calibrated using a 10 mm cell filled with methyl isobutyl ketone with the sample shutter in the open position.

A comparison of methyl isobutyl ketone with the alkyd - MIBK solution used in the turbidity titration method shows less than 1% difference in Transmittance when used to calibrate the ultraviolet visible spectrophotometer to 100% Transmittance. The % Transmittance is measured on the ultraviolet visible spectrophotometer in the same manner and using the same conditions as described for the turbidimetric titration method.

Titration of the sample is then continued by addition of the calculated volume of methyl alcohol as given by Equation 2 to yield a solvent blend equal to $D_i = 1.50$.

<u>Equation 4</u>

$$Y = .6364x$$

where

Y = volume (mls) of methyl alcohol to yield solvent $Di_{1.5}$

X = volume (mls) of solution $Di_{2.2}$ added to sample (as calculated by Equation 3).

The % Transmittance of the sample solution is then measured on the spectrophotometer and recorded as $\%T_{1.5}$.

A full description of this method for determining molecular characteristics of alkyd resins is presented in the proposed test procedure (Appendix, page 89).

Data obtained by this procedure is given in the Appendix, Table X. All samples tested had been evaluated by the turbidimetric titration method and 16 had been analyzed previously by gel permeation chromatography. Graph 10 illustrates the correlation existing between the distribution index and the % Transmittance for alkyds evaluated with solution $Di_{2.2}$. Alkyds having distribution indices greater than 2.2 exhibit a % Transmittance less than 8%. These alkyds are known to produce abnormally high viscosities in traffic paint.

Similarly, Graph 11 illustrates the data for alkyds evaluated with solution $Di_{1.50}$ and shows that an alkyd having a D_i value less than 1.50 exhibits a % Transmittance greater than 70%. Information compiled reveals that these alkyds produce traffic paint with abnormally low viscosities.

Thus, data obtained using this test procedure is directly related to the information obtained by the turbidimetric titration method and provides an effective means of characterizing the alkyd polymer.

ACKNOWLEDGEMENTS

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BIBLIOGRAPHY

1. Patton, Temple C., Official Digest, Vol. 32, No. 430, pp. 1544-1556, November, 1960.

2. Flory, P. J., Principles of Polymer Chemistry, p. 345, (Cornell University Press, Ithaca and London, 1953).

3. Schneider, Nathaniel S., Journal of Polymer Science, Part C, No. 8, pp. 179-204.

4. Billmeyer, Fred W., Jr., Textbook of Polymer Science, p. 50, (John Wiley & Sons, Inc., New York, 1962).

5. Flory, P. J., Reference 2.

6. Bartosiewicz, R. L., Journal of Paint Technology, Vol. 39, No. 504, pp. 28-39, January, 1967.

7. Billmeyer, Fred W., Jr., Journal of Paint Technology, Vol. 41, No. 528, pp. 2-16, January, 1969.

8. Rybicka, S. M., Olley, R. H., and Cronin, P. J., Journal of Chromatographic Science, Vol. 9, pp. 424-7, July, 1971.

9. Rudin, A. and Johnston, H. K., Journal of Paint Technology, Vol. 43, No. 559, pp. 39-47, August, 1971.

10. Hillyer, M. J. and Leonard, W. J., American Chemical Society, Division of Organic Coatings and Plastics Chemistry (Papers presented at Washington Meeting, 163rd Meeting), Vol. 31, No. 2, pp. 390-400, September, 1971.

11. Berger, H. W., Journal of Paint Technology, Vol. 39, No. 508, pp. 310-5, May, 1967.

12. Ivanfi, J. and Ady, E., Journal of Paint Technology, Vol. 42, No. 542, pp. 199-213, March, 1970.

13. Flory, P. J., Reference 2, p. 296.

14. Billmeyer, F. W., Reference 4, p. 67.

15. Rybicka, S. M., Olley, R. H., and Cronin, P. J., Reference 8, pp. 425-6.

16. Ivanfi, J. and Ady, E., Reference 12, p. 200.

17. Ibid., p. 200.

18. Chicago Society for Paint Technology, *Official Digest*, Vol. 33, No. 434, Part 2, p. 40, March, 1971.

19. Golden Gate Society for Coatings Technology, *Journal of Paint Technology*, Vol. 40, No. 527, P. 588, December, 1968.

20. Ivanfi, J. and Ady, E., Reference 12, p. 200.

21. Rybicka, S. M., et al, Reference 8, p. 424.

22. Hillyer, M. J. and Leonard, W. J., Reference 10, pp. 390-1.

23. Flory, P. J., Reference 2, p. 345.

24. Hillyer, M. J. and Leonard, W. J., Reference 10, p. 392.

APPENDIX

SAMPLE CALCULATION

Calculations are based on data
from titration in Figure 1

Reading No.	V*	$\frac{1}{V}$	$\log \frac{1}{V}$
1	192.0	2.042	.3101
2	196.0	2.020	.3054
3	200.0	2.000	.3010
4	204.0	1.980	.2967
5	208.0	1.962	.2927
6	212.0	1.943	.2885
7	216.0	1.926	.2847
8	220.0	1.909	.2808
9	224.0	1.893	.2772
10	228.0	1.877	.2735
11	236.0	1.847	.2665
12	244.0	1.820	.2601

* V = volume of precipitating agent (methyl alcohol) added.

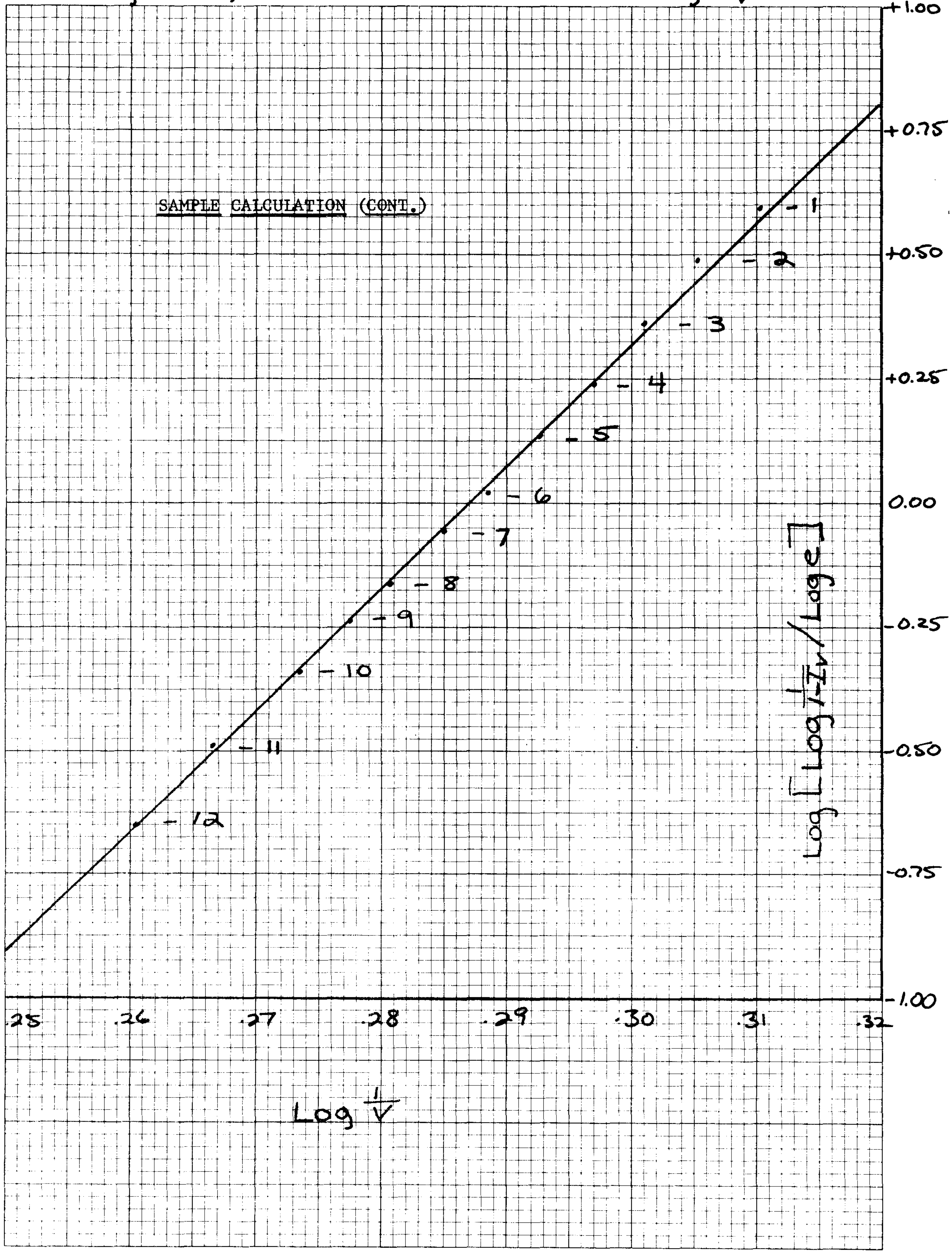
SAMPLE CALCULATION
(CONT.)

Reading No.	T	$1-I_V$	$\frac{1}{1-I_V}$	$\log \frac{1}{1-I_V}$	$\log \frac{1}{1-I_V}/\log e$	$\log \frac{\log 1-I_v}{\log e}$
1	.980	.020	50.0	1.6990	3.912	.5924
2	.952	.048	20.8	1.3181	3.035	.4822
3	.897	.103	9.71	.9872	2.273	.3566
4	.826	.174	5.74	.7589	1.747	.2423
5	.740	.260	3.85	.5855	1.348	.1297
6	.652	.348	2.87	.4579	1.054	.0228
7	.580	.420	2.38	.3766	.8671	-.0619
8	.493	.507	1.97	.2945	.6781	-.1687
9	.437	.563	1.78	.2504	.5766	-.2384
10	.367	.633	1.58	.1987	.4575	-.3496
11	.276	.724	1.38	.1399	.3221	-.4920
12	.200	.800	1.25	.0969	.2231	-.6515

The plot of $\log \frac{1}{V}$ versus $\log \left[\log \frac{1}{1-I_V}/\log e \right]$ is shown. Determination of the slope of line obtained yields the value for "a" and the "y" intercept yields the value for "b" given in Equation 1.

SAMPLE CALCULATION (CONT.)

$\text{Log}\left[\text{Log}\frac{1}{1-I_v}/\text{Log } e\right]$ vs. $\text{Log}\frac{1}{V}$



SAMPLE CALCULATION
(CONT.)

$$\text{slope} = b = \frac{\log \frac{1}{V}}{\log \left[\log \frac{1}{1-I_V} / \log e \right]}$$

$$= \frac{+.75 - (-.75)}{.3180 - .2565}$$

$$= \frac{1.50}{.0615}$$

$$b = 24.4$$

for the point #8 on the line, the values for log $\log \frac{1}{1-I_V}/\log e$, $\log \frac{1}{V}$, and "b" are substituted into Equation 1 to determine the value for "a".

$$\log a = \log \left[\log \frac{1}{1-I_V}/\log e \right] - b \log \frac{1}{V}$$

$$\log a = -.1687 - 24.4\ (.2808)$$

$$= -.1687 - 6.8515$$

$$= -7.0202$$

$$-\log a = 7.0202$$

$$a = 9.55 \times 10^{-8}$$

knowing the parameters "a" and "b", one can calculate the value $\frac{dI_V}{d_V}$ for each volume increment (Equation 2) and thereby obtain data necessary to plot the distribution curve.

thus:

$$a \cdot b = (9.55 \times 10^{-8}) \quad (24.4)$$

and

$$= 2.33 \times 10^{-6}$$

$$b - 1 = 23.4 \times 10^{-6}$$

SAMPLE CALCULATION
(CONT.)

The following table shows the results obtained for $\frac{d^{I_v}}{d_V}$:

Reading No.	$\frac{1}{V}^{b-1}$	$\frac{1}{V}^{b}$	$a \cdot b \frac{1}{V}^{b-1}$	$e^{a} \frac{1}{V}^{b-1}$	$\frac{a\ I_V}{d_V}$
1	1.80×10^7	3.59×10^7	41.9	30.8	1.36
2	1.40×10^7	2.83×10^7	32.6	14.9	2.19
3	1.11×10^7	2.21×10^7	25.9	8.25	3.14
4	8.77×10^6	1.74×10^7	20.4	5.27	3.87
5	7.07×10^6	1.39×10^7	16.5	3.77	4.38
6	5.64×10^6	1.10×10^7	13.1	2.86	4.58
7	4.59×10^6	8.84×10^6	10.7	2.33	4.59
8	3.72×10^6	7.10×10^6	8.67	1.97	4.40
9	3.07×10^6	5.80×10^6	7.15	1.74	4.11
10	2.51×10^6	4.71×10^6	5.85	1.57	3.73
11	1.72×10^6	3.18×10^6	4.01	1.36	2.95
12	1.22×10^6	2.22×10^6	2.84	1.24	2.29

A plot of $d^{I_v}/d_V \times 10^2$ versus $\frac{1}{V}$ yields the differential distribution curve for the alkyd.

SAMPLE CALCULATION (CONT.)

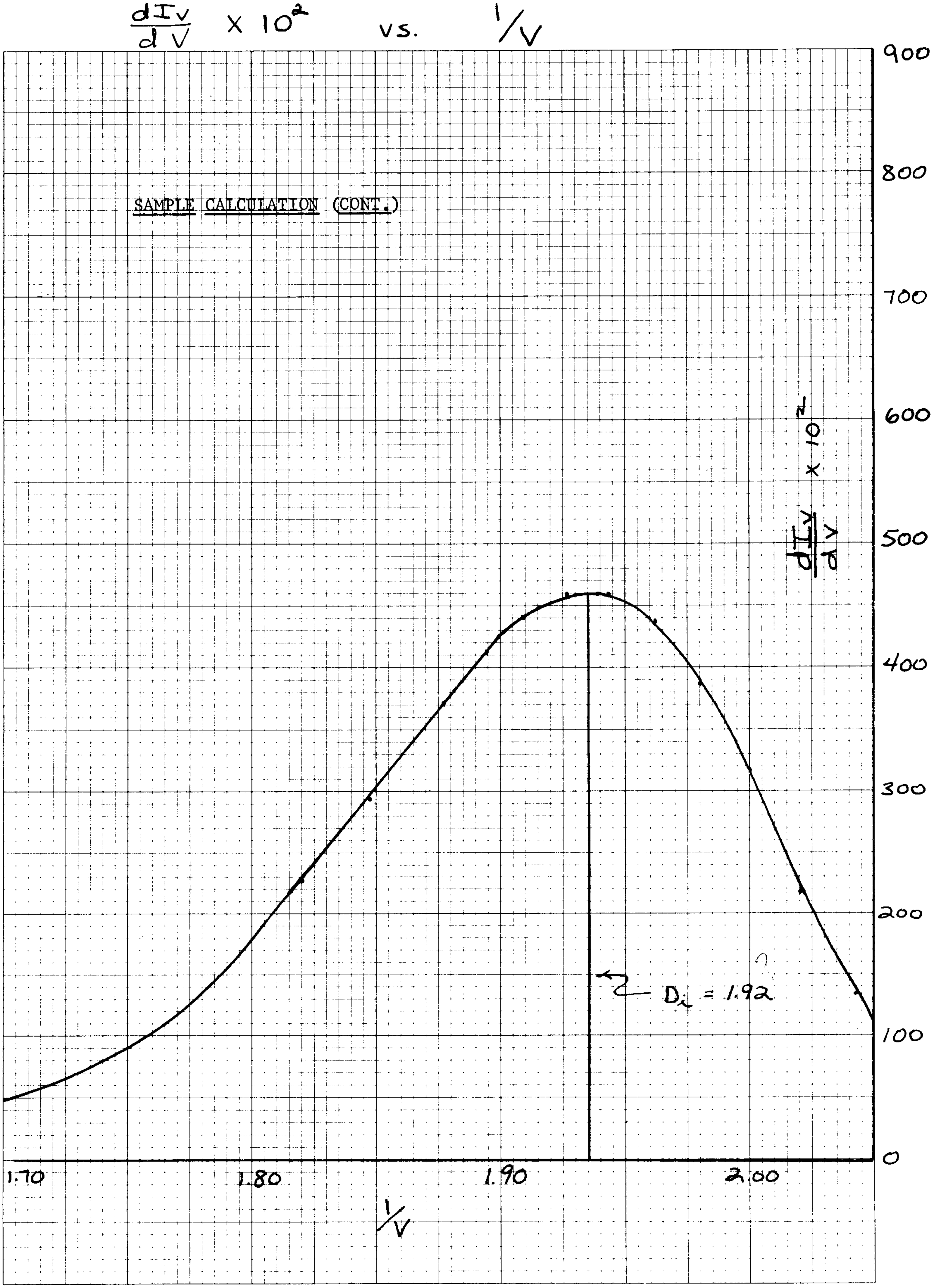


TABLE I

Spectrophotometric parameters adopted in turbidimetric titration method for determination of distribution curves for alkyd resins.

Instrument: Beckman DK-2A, Ultraviolet Visible Spectrophotometer

Operating mode: Energy-level single beam
Wavelength (λ) = 750 mm
Sensitivity setting = 50
Time constant = .6
Slit opening = .1 mm
Cell (pyrex) - Beckman 75152
Pathlength of cell = 10.0 mm

TABLE II

TURBIDIMETRIC TITRATION DATA AND CALCULATED VALUES FOR DISTRIBUTION INDEX

Sample No.	Volume of Methanol*	D_i
10	187	2.07
13	177	2.13
55	182	2.10
67	322	1.62
74	444	1.45
75	339	1.59
76	400	1.50
77	385	1.52
78	255	1.78
79	200	2.00
80	200	2.00
81	270	1.74
82	146	2.37
83	148	2.35
84	161	2.24
85	268	1.75
86	185	2.08
87	327	1.61
88	155	2.29
89	194	2.03
90	192	2.04
91	210	1.95
93	137	2.46
94	188	2.06
96	121	2.65
97	218	1.92
98	210	1.95
99	131	2.53
100	500	1.41
101	500	1.41
102	184	2.09
103	286	1.70
104	184	2.09
105	350	1.57
106	174	2.15
108	175	2.14
109	256	1.79
110	171	2.17

(Cont. next page)

TABLE II

TURBIDIMETRIC TITRATION DATA AND CALCULATED VALUES FOR DISTRIBUTION INDEX

Sample No.	Volume of Methanol*	D_i
111	370	1.54
112	190	2.05
113	440	1.45
114	351	1.57
115	184	2.09
116	174	2.15
117	238	1.84
119	372	1.54
120	184	2.09
121	177	2.13
122	148	2.35
136	206	1.97
144	234	1.85
145	308	1.65
148	187	2.07
149	194	2.03
150	212	1.94

* Volume recorded at max. $\frac{dI_v}{d_V}$ of differential distribution curve (See Sample Calculations).

TABLE III

Sample No.	Product	Theoretical Wt/gal. ± .05	Required Viscosity Range	Actual Wt/gal.	Actual Viscosity	D_i
10	Pre-Sample					2.07
13	Pre-Sample					2.13
55	Pre-Sample					2.10
67	YPT-7	12.04	80 - 90	12.08	77	1.62
74	WPT-8	11.92	70 - 80	11.90	65	1.45
75	WPT-8	11.92	70 - 80	11.89	69	1.59
76	YPT-8	12.49	72 - 82	12.75	68	1.50
77	Pre-Sample					1.52
78	WPT-7b	11.06	72 - 82	11.17	70	1.78
79	YPT-8	12.44	72 - 82	12.41	77	2.00
80	WPT-8	11.98	70 - 80	11.98	76	2.00
81	WPT-8	11.99	70 - 80	12.05	70	1.74
82	YPT-8	12.50	72 - 82	12.49	87	2.37
83	YPT-8	12.49	72 - 82	12.55	85	2.35
84	Pre-Sample					2.24
85	WPT-8	11.93	70 - 80	11.93	71	1.75
86	YPT-8	11.52	72 - 82	12.47	78	2.08
87	YPT-7	12.07	80 - 90	12.05	83	1.61
	WPT-7b	10.99	72 - 82	10.98	73	1.61
88	YPT-8	12.50	72 - 82	12.49	84	2.29
89	YPT-8b	12.60	70 - 80	12.58	76	2.03
90	YPT-7	12.07	80 - 90	12.10	86	2.04
91	YPT-8b	12.60	70 - 80	12.56	72	1.95
93	WPT-8b	11.97	70 - 80	11.95	88	2.46
94	YPT-8b	12.61	70 - 80	12.59	76	2.06
96	WPT-8	11.97	70 - 80	11.96	88	2.65
97	WPT-8b	11.99	70 - 80	12.01	74	1.92
98	WPT-8b	11.99	70 - 80	11.99	71	1.95
99	WPT-8b	11.94	70 - 80	11.91	85	2.53
100	Pre-Sample					1.41
101	WPT-8	11.96	70 - 80	12.00	69	1.41
102	WPT-8	11.97	70 - 80	11.98	77	2.09
103	YPT-8b	12.54	70 - 80	12.52	71	1.70
104	WPT-8b	11.99	70 - 80	11.94	78	2.09

TABLE III
(CONT.)

Sample No.	Product	Theoretical Wt/gal. ± .05	Required Viscosity Range	Actual Wt/gal.	Actual Viscosity	D_i
105	WPT-7b	11.14	72 - 82	11.15	68	1.57
106	YPT-8b	12.52	70 - 80	12.54	81	2.15
	WPT-8b	11.99	70 - 80	11.97	80	2.15
107	YPT-8b	12.52	70 - 80	12.54	83	2.14
109	WPT-8b	12.08	70 - 80	12.07	72	1.79
110	YPT-8b	12.62	70 - 80	12.57	81	2.17
111	WPT-7b	11.09	72 - 82	11.14	69	1.54
112	YPT-8b	12.62	70 - 80	12.61	81	2.05
113	YPT-8b	11.96	70 - 80	11.97	68	1.45
114	WPT-8b	12.01	70 - 80	12.02	69	1.57
115	YPT-8b	12.52	70 - 80	12.53	80	2.09
116	YPT-8b	12.52	70 - 80	12.48	83	2.15
117	YPT-8b	12.52	70 - 80	12.53	78	1.84
119	WPT-8b	12.08	70 - 80	12.10	72	1.54
120	YPT-8b	12.52	70 - 80	12.48	78	2.09
121	YPT-8b	12.51	70 - 80	12.46	80	2.13
122	Pre-Sample					2.35
136	YPT-8b	12.50	70 - 80	12.51	75	1.97
144	YPT-8b	12.50	70 - 80	12.50	73	1.85
145	WPT-8b	12.07	70 - 80	12.09	70	1.65
148	WPT-8b	12.02	70 - 80	11.95	80	2.07
149	WPT-8b	12.04	70 - 80	11.98	76	2.03
	YPT-8b	12.61	70 - 80	12.59	75	2.03
150	YPT-8b	12.58	70 - 80	12.52	73	1.94

TABLE IV

EXPERIMENTAL TRAFFIC PAINT FORMULAS

Formula A

	Grams
Medium Chrome Yellow, 1238, Mineral Pigment	80
TiO_2, FF, Du Pont	10
Lead Free Zinc Oxide, AZO-33	20
Talc, 325, International	70
Calcium Carbonate, Snowflake, T-W	80
Bentone 38	0.8
Methyl Alcohol	2.0
*Traffic Alkyd, 60% Solids	59.3
Chlorinated Rubber, X-20, Alloprene	35.6
Chlorinated Paraffin, 42, Cerechlor	30.0
24% Lead Drier	0.8
6% Cobalt Drier	0.4
Anti-Skinning Agent	1.2
Epichlorohydrin	1.2
Methyl Amyl Acetate	14.0
Methyl Ethyl Ketone	103.1

Formula B

	Grams
Medium Chrome Yellow, 1238, Mineral Pigment	80
TiO_2, FF, Du Pont	10
Lead Free Zinc Oxide, AZO-33	20
Talc, 325, International	70
Calcium Carbonate, Snowflake, T-W	80
Bentone 38	0.8
Methyl Alcohol	2.0
*Traffic Alkyd, 60% Solids	39.5
Chlorinated Rubber, X-20, Alloprene	47.4
Chlorinated Paraffin, 42, Cerechlor	30.0
24% Lead Drier	0.8
6% Cobalt Drier	0.4
Anti-Skinning Agent	1.2
Epichlorohydrin	1.2
Methyl Amyl Acetate	14.0
Methyl Ethyl Ketone	111.0

TABLE IV

EXPERIMENTAL TRAFFIC PAINT FORMULAS
(CONT.)

Formula C

	Grams
Medium Chrome Yellow, 1238, Mineral Pigment	80
TiO_2, FF, Du Pont	10
Lead Free Zinc Oxide, AZO-33	20
Talc, 325, International	70
Calcium Carbonate, Snowflake, T-W	80
Bentone 38	0.8
*Traffic Alkyd, 60% Solids	118.7
Chlorinated Paraffin, 42, Cerechlor	30.0
24% Lead Drier	0.8
6% Cobalt Drier	0.4
Anti-Skinning Agent	1.2
Epichlorohydrin	1.2
Methyl Amyl Acetate	14.0
Methyl Ethyl Ketone	79.3

* Alkyds used in these formulas were numbers 76, 88, 97, 110 and 145. Reference is made to Table III for the data on YPT-8 and YPT-8b viscosities.

The following table shows viscosities (expressed in KU's) obtained from the three modified traffic paint formulas using selected alkyd resins with distribution indices ranging from 1.50 - 2.29.

	Alkyd Resin Sample Number	76	88	97	110	145
Traffic Paint Formula	YPT-8b	68	84	74	81	70
	A	68	84	80	86	72
	B	68	93	88	93	82
	C	57	64	61	64	58

TABLE V

INFRARED DATA

Sample	Absorbance$_{3540}$	Absorbance$_{2960}$	$A_{3540} + A_{2960}$	$\frac{A_{2960}}{A_{3540} + A_{2960}}$	D_i
59	.0200	.5272	.5472	.964	2.49
67	.0602	.6021	.6623	.909	1.62
74	.0667	.5247	.5914	.887	1.45
76	.0671	.4999	.5670	.882	1.50
78	.0564	.4634	.5198	.891	1.76
81	.0463	.4357	.4820	.904	1.74
82	.0224	.4742	.4966	.955	2.37
88	.0298	.5329	.5627	.947	2.29
94	.0420	.6020	.6440	.935	2.06
121	.0326	.4584	.4910	.934	2.13
122	.0141	.3881	.4022	.965	2.35
148	.0286	.3984	.4270	.933	2.07
149	.0385	.4781	.5166	.925	2.03
151	.0348	.3508	.3856	.910	1.79
152	.0330	.3793	.4123	.920	1.92
153	.0427	.3882	.4309	.901	1.68
67	.0613	.6016	.6629	.908	1.62

TABLE VI

CALIBRATION DATA FOR G.P.C. ANALYSIS

GROUP I

Code	Supplier	M_w	M_n	Elution Count
41983	WA	-	9881	22.87
41985	WA	-	5170	24.48
25169	WA	5000	4600	24.06
41994	WA	-	3200	25.02
41993*	WA	-	2070	26.16
52a	PC	19,800 - 19,900 ± 2%	19,800 ± 3%	21.65
54a	PC	96,200 ± 2%	97,600 ± 5%	19.63
57a	PC	50,500 ± 2%	50,500 ± 5%	20.28

GROUP II

Code	Supplier	M_w	M_n	Elution Count
51a	PC	-	160,000	23.32
52a	PC	19,800 - 19,900 ± 2%	19,800 ± 3%	28.00
54a	PC	96,200 ± 2%	97,600 ± 5%	25.75
25169	WA	5000	4600	31.05
41993*	WA	-	2070	32.60

* Polyglycol standard converted to equivalent polystyrene standard.

TABLE VII

G.P.C. DATA FOR CALCULATING

% POLYMER > 12,000 MOLECULAR WEIGHT UNITS

Sample No.	Group	Cum H_i up to Mol. Wt. 12,000	ΣH_i	% Polymer < Mol. Wt. 12,000	D_i	% Polymer > Mol. Wt. 12,000
10	2	231.5	434.4	53.29	2.07	46.71
13	2	220.4	416.2	52.93	2.13	47.07
55_I	1	295.1	560.7	52.63	2.10	47.37
55_{II}	2	89.0	164.8	54.00	2.10	46.00
76	1	119.1	149.9	79.45	1.50	20.55
78	2	152.1	231.1	68.24	1.78	31.76
80	2	112.7	193.5	58.24	2.00	41.76
81	1	115.6	189.9	60.87	1.74	39.13
82	1	248.2	476.8	52.05	2.37	47.95
87	1	268.5	386.5	69.46	1.61	30.54
88	1	99.8	197.4	50.55	2.29	49.45
96	1	174.7	346.4	50.43	2.65	49.57
111	1	136.4	201.3	67.75	1.54	32.25
113	1	377.7	496.5	76.07	1.45	23.93
116	1	269.9	488.1	55.29	2.15	44.71
117	2	107.7	187.6	57.40	1.84	42.60
122	2	110.4	203.9	54.14	2.35	45.86
144	2	150.2	228.8	65.43	1.85	34.57
145	2	148.0	223.6	66.18	1.65	33.82

Group 1 readings taken at count 22.5

Group 2 readings taken at count 29.0

TABLE VIII

G.P.C. DATA FOR CALCULATING VALUES OF MOLECULAR WEIGHT CORRESPONDING TO D_i

Sample No.	Group	D_i	Vol_{Tot}	f*	H_i	f H_i	Corresp. Count No.	Mol. Wt.
10	2	2.07	386.8	.3998	434.4	173.7	30.4	6100
13	2	2.13	376.9	.4152	416.2	172.8	30.4	6100
55a	1	2.10	381.8	.4076	560.7	228.5	23.6	6000
55b	2	2.10	381.8	.4076	164.8	67.17	30.6	6300
76	1	1.50	600.0	.0690	149.9	10.3	27.3	1300
78	2	1.78	456.4	.2918	231.1	67.43	32.0	2900
80	2	2.00	400.0	.3793	193.5	73.4	31.0	4600
81	1	1.74	470.3	.2702	189.9	51.31	25.2	2800
82	1	2.37	346.0	.4631	476.8	220.8	23.0	8700
87	1	1.61	527.9	.1808	386.5	69.88	25.9	2100
88	1	2.29	355.0	.4491	197.4	88.65	23.0	8700
96	1	2.65	321.2	.5016	346.4	173.8	22.5	12,000
111	1	1.54	570.4	.1149	201.3	23.13	26.3	1750
113	1	1.45	644.4	0.000	496.5	0	28.0	1100
116	1	2.15	373.9	.4198	488.1	204.9	23.6	5900
117	2	1.84	438.0	.3203	187.6	60.09	31.5	3700
122	2	2.35	348.1	.4599	203.9	93.77	30.0	8700
144	2	1.85	435.3	.3245	228.8	74.24	31.8	3400
145	2	1.65	507.7	.2122	223.6	47.45	32.4	2420

$$*f = 100 - \frac{\text{Vol. total}}{644.4}$$

TABLE IX

COMPATIBILITY DATA FROM G.P.C.

Sample No.	% Polymer $\leq$ 2000 M_w	% Polymer $\geq$ 7000 M_w	Comp_i	Results
10	11.2	26.9	2.40	Fail
13	8.9	27.4	3.1	Fail
55_1	10.8	24.6	2.28	Fail
55_2	10.8	25.0	2.31	Fail
76	21.6	2.3	0.11	Pass
78	12.0	7.7	0.64	Pass
80	9.2	17.2	1.9	Pass
81	4.9	6.7	1.4	Pass
82	13.7	15.5	1.13	Pass
87	11.5	0.45	.04	Pass
88	9.3	26.0	2.8	Marginal
96	12.6	28.2	2.24	Marginal
111	14.2	5.36	0.38	Pass
113	15.0	0.31	0.02	Pass
116	11.3	12.9	1.14	Pass
117	10.5	21.0	2.00	Pass
122	9.7	23.1	2.4	Pass
144	11.2	9.5	0.85	Pass
145	9.0	11.2	1.2	Pass

% Polymer $\geq$ 7000 M_w and

% Polymer $\leq$ 2000 M_w computed from cumulative curves

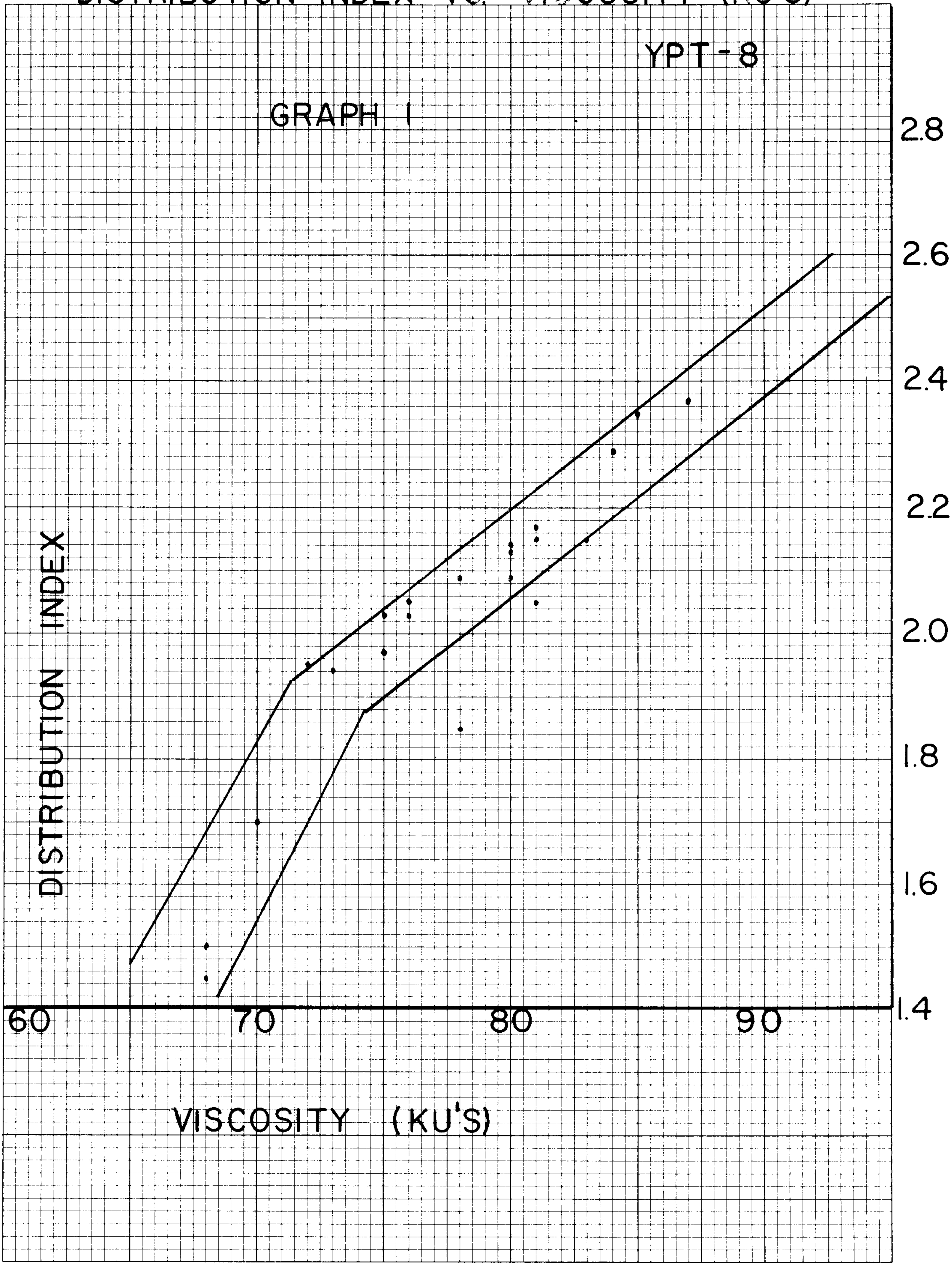
$$\text{Comp}_i = \text{Compatibility Index} = \frac{\%\ \text{Polymer} \geq 7000\ M_w}{\%\ \text{Polymer} \leq 2000\ M_w}$$

TABLE X

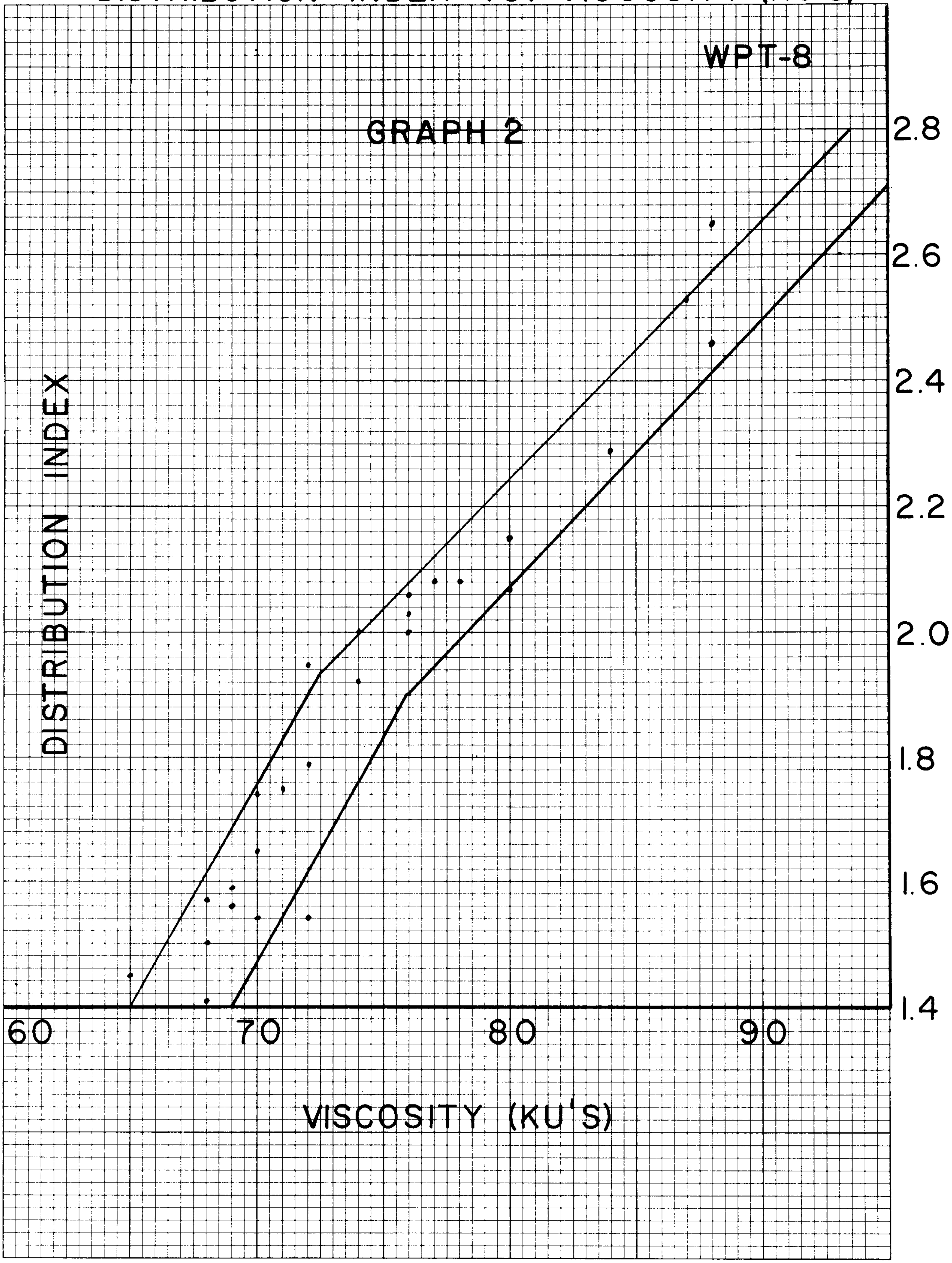
DATA OF SAMPLES TESTED ACCORDING TO PROPOSED METHOD FOR DETERMINATION OF MOLECULAR CHARACTERISTICS OF TRAFFIC ALKYD RESINS BY TURBIDIMETRIC MEASUREMENTS

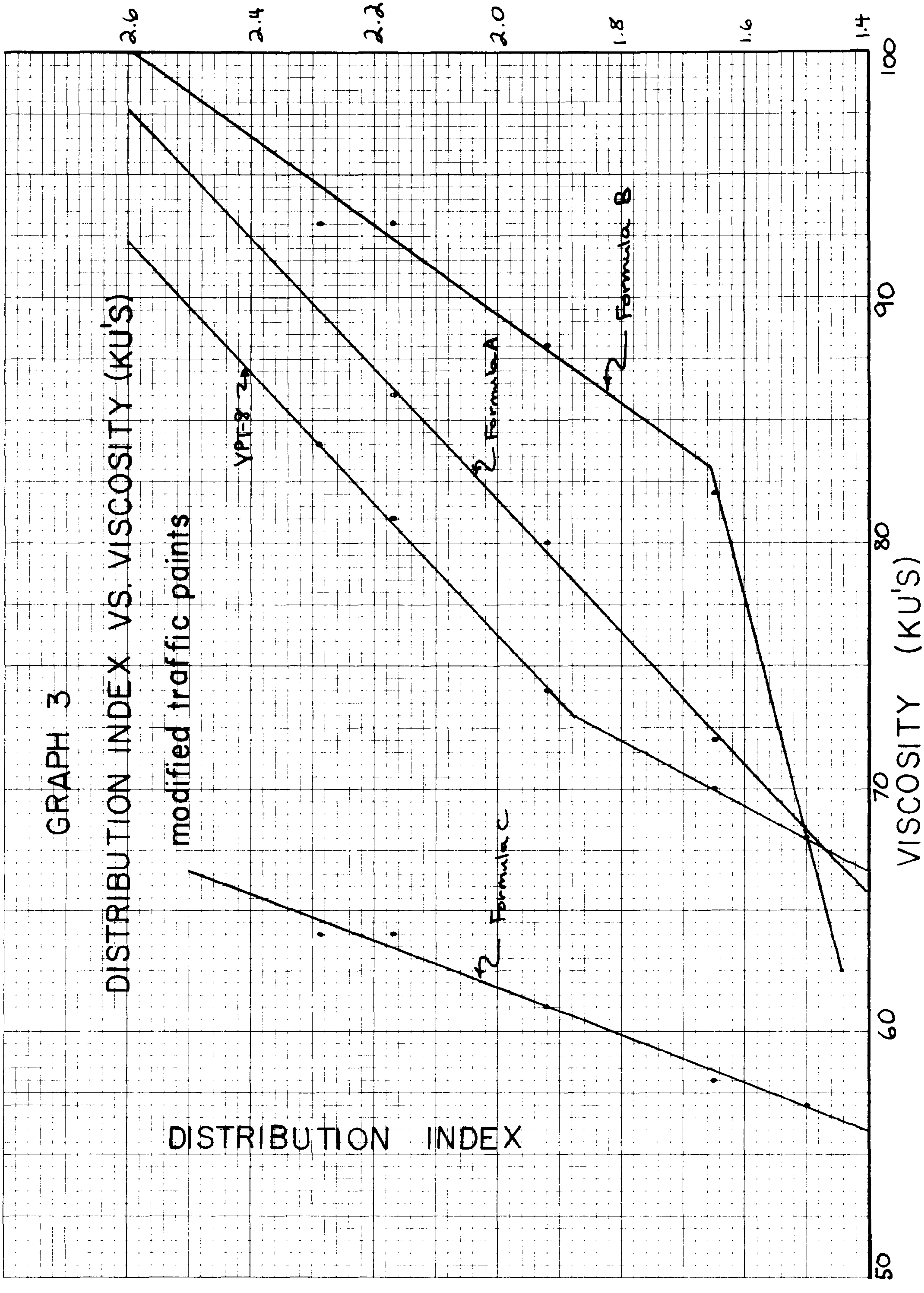
Sample No.	D_i	NVM	$\%T_{2.2}$	$\%T_{1.5}$
10	2.07	59.3	99.9	4.5
13	2.13	58.8	64.1	0.3
55	2.10	59.2	97.9	4.0
74	1.45	60.8	99.3	91.2
76	1.50	62.0	99.8	98.8
78	1.78	63.6	98.9	14.9
80	2.00	60.9	98.0	0.0
81	1.74	60.2	99.9	8.5
82	2.37	60.6	3.4	0.0
84	2.24	61.0	2.4	0.0
87	1.61	60.9	99.2	22.7
88	2.29	60.3	0.6	0.0
96	2.65	59.6	0.0	0.0
100	1.41	62.2	99.9	79.8
101	1.41	59.8	99.6	89.8
106	1.41	59.1	99.2	0.2
110	2.17	59.6	9.6	0.0
111	1.54	45.8	99.8	44.0
113	1.45	60.0	99.0	83.7
118	1.54	55.5	99.8	32.4
122	2.35	59.4	1.6	0.0
144	1.85	60.4	96.9	2.6
145	1.65	55.7	99.2	14.6

DISTRIBUTION INDEX VS. VISCOSITY (KU'S)



DISTRIBUTION INDEX VS. VISCOSITY (KU'S)

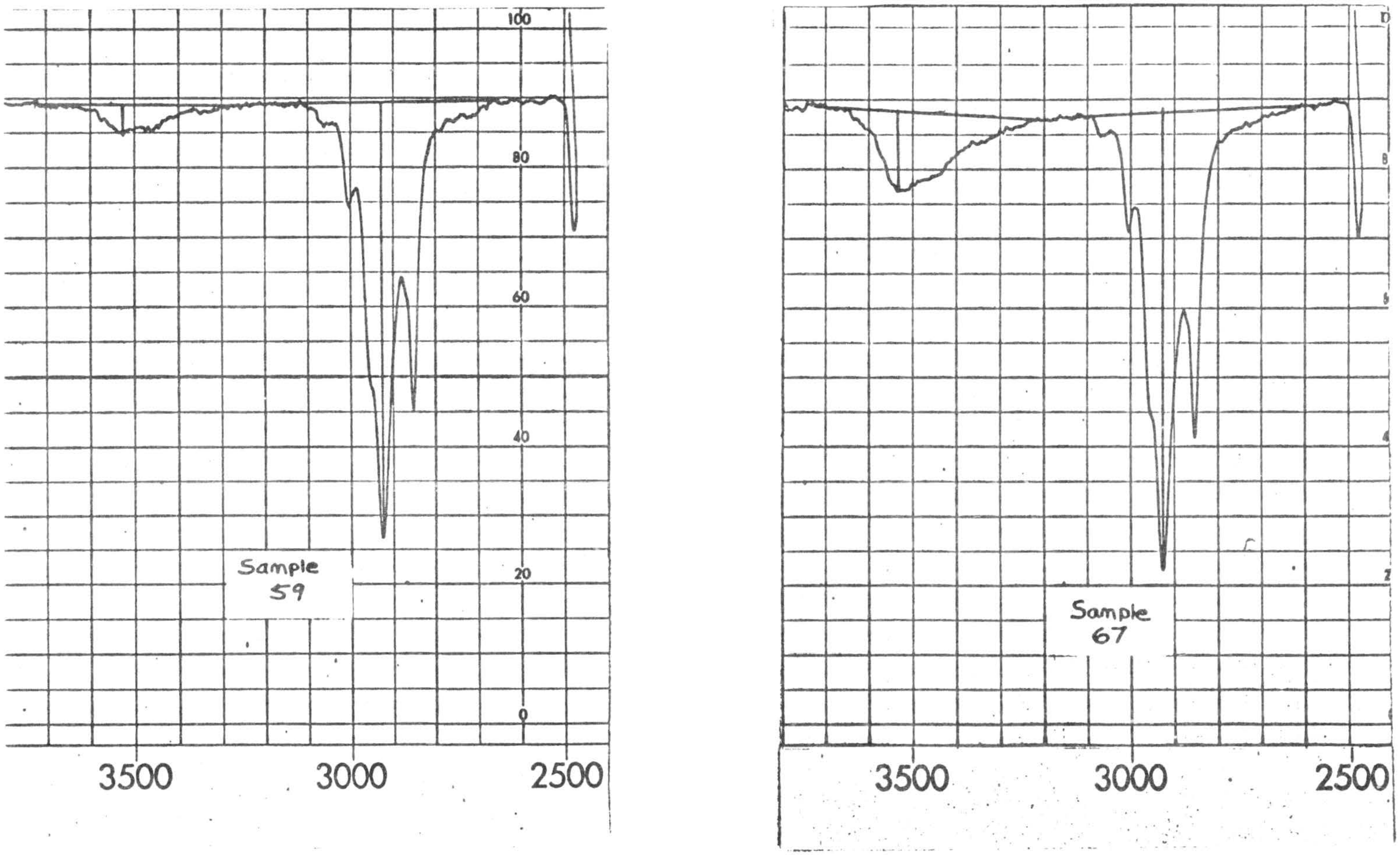




GRAPH 3

DISTRIBUTION INDEX VS. VISCOSITY (KU'S)

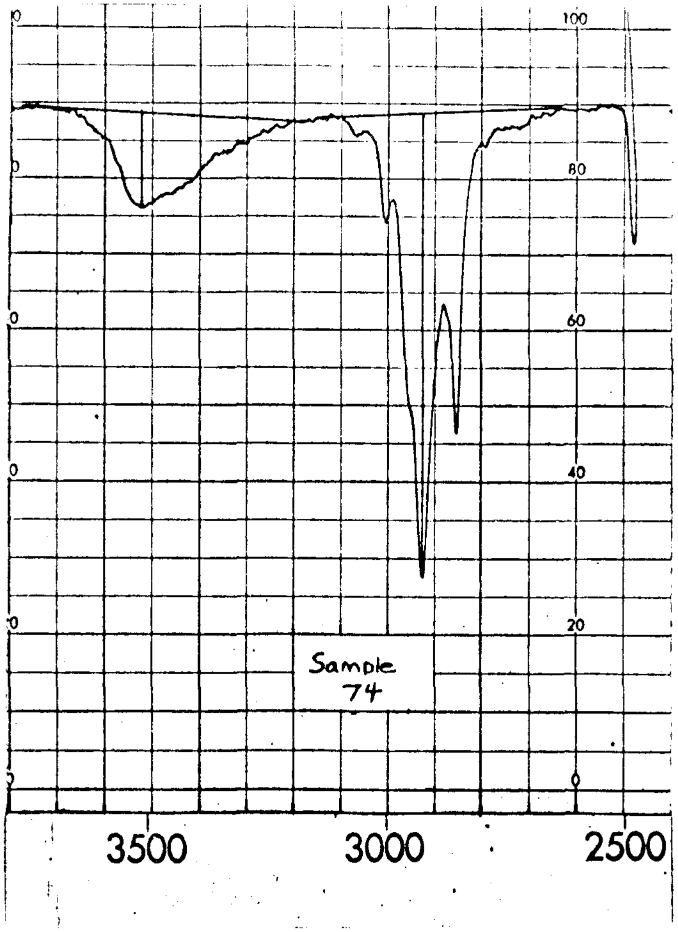
modified traffic paints



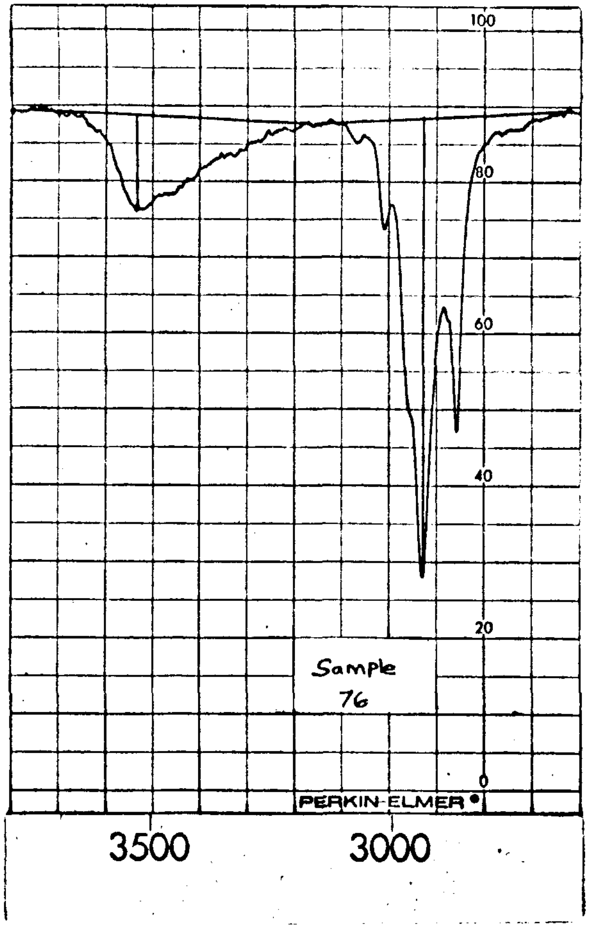
Graph 4a

Graph 4b

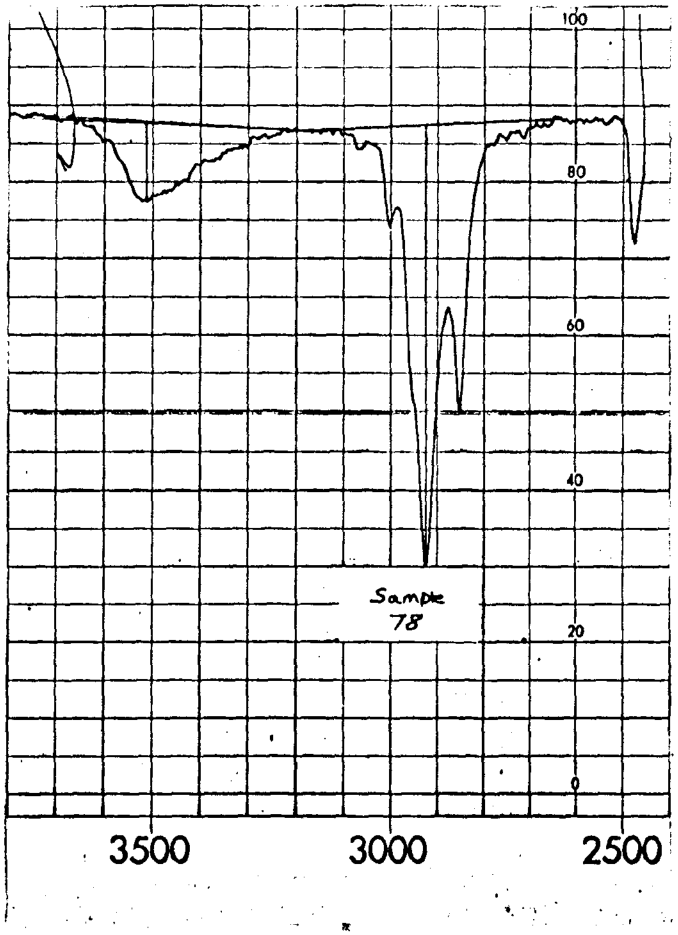
Infrared Spectra of Alkyd Resins



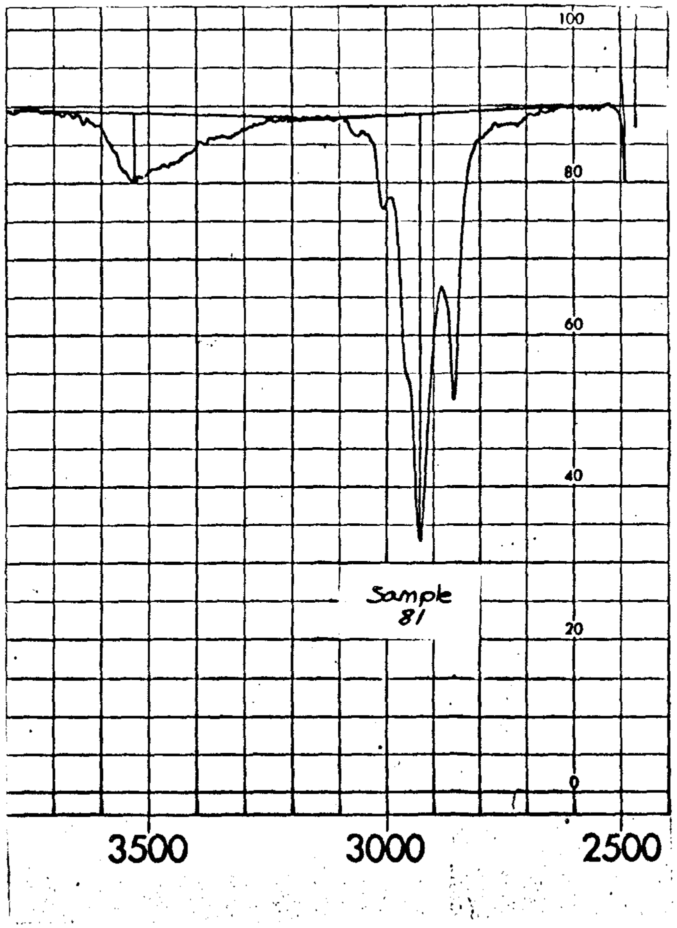
Graph 4c



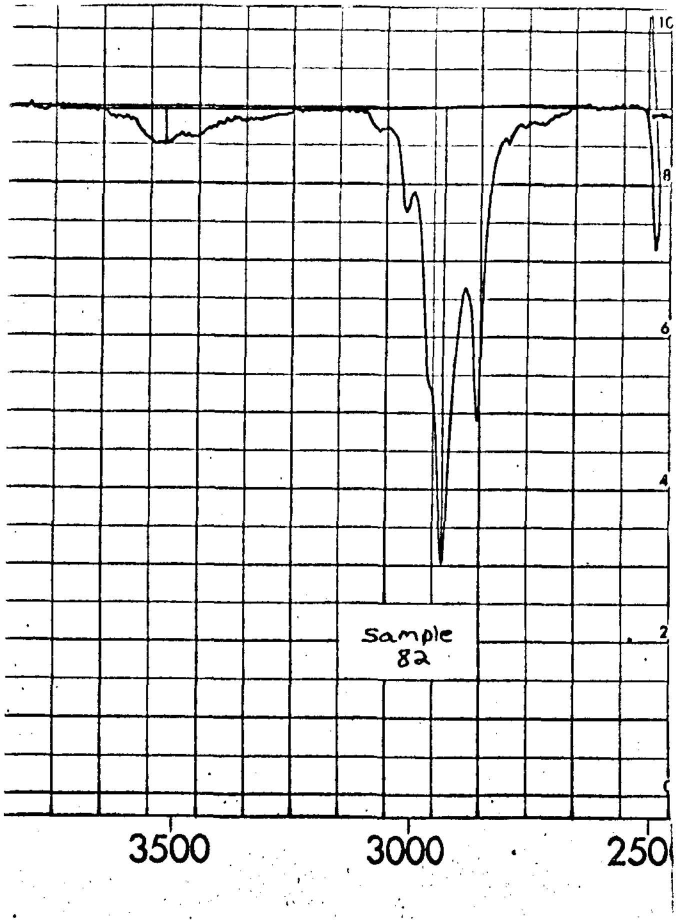
Graph 4d



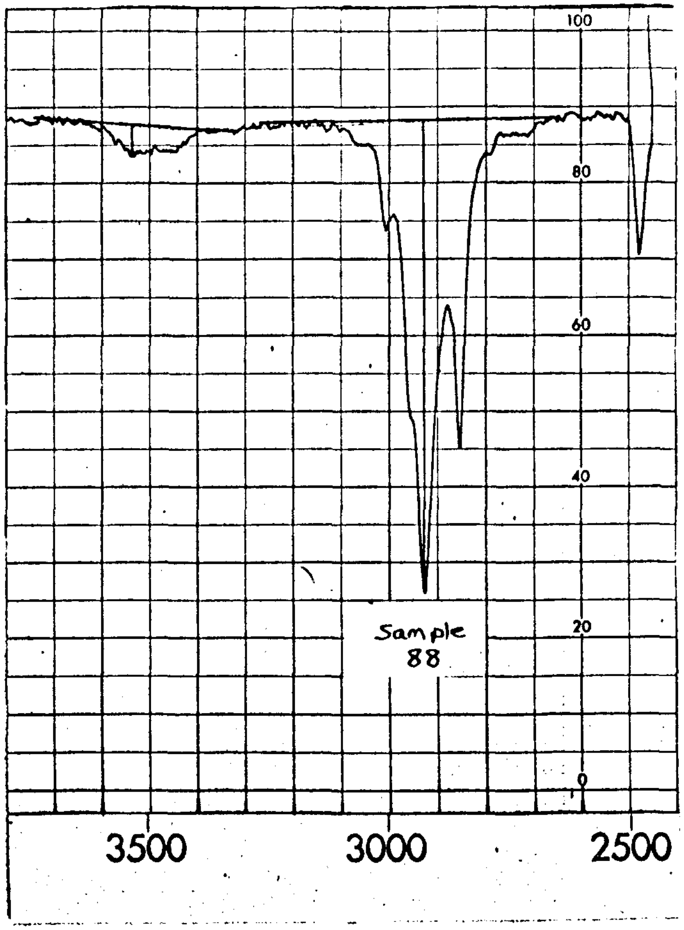
Graph 4e



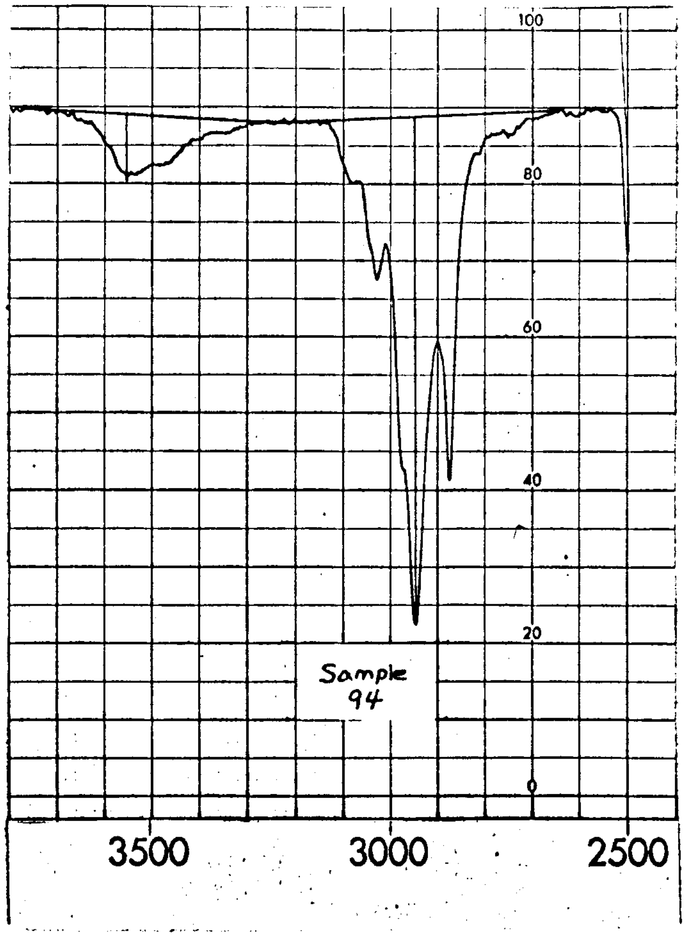
Graph 4f



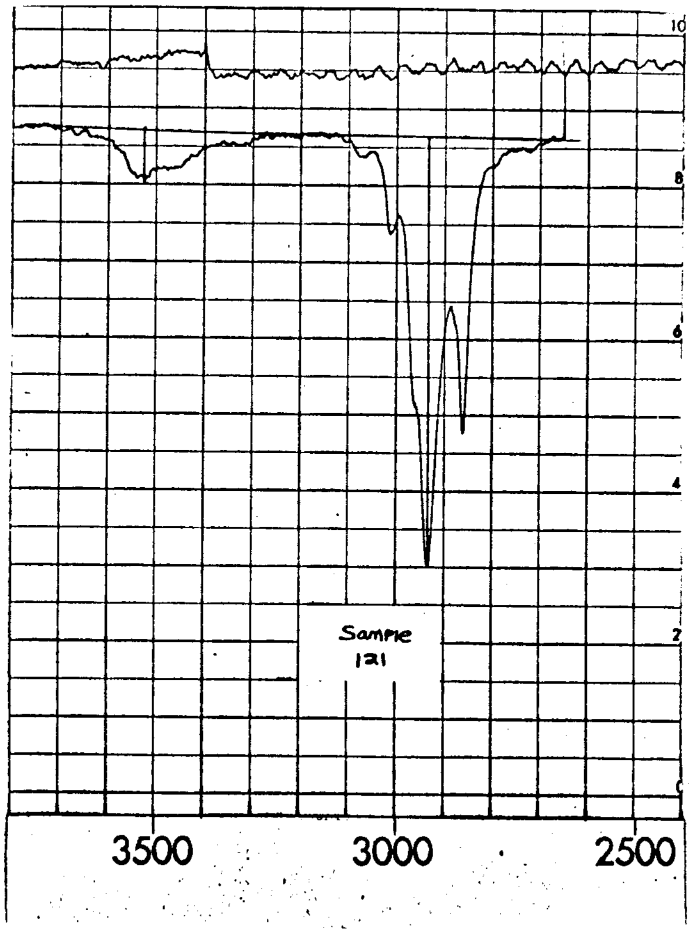
Graph 4g



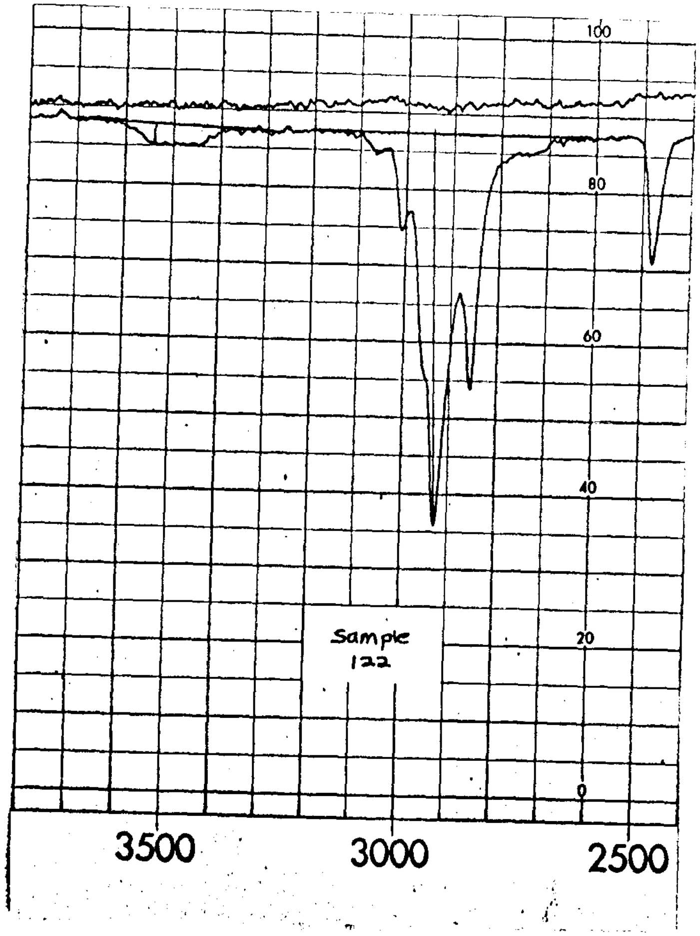
Graph 4h



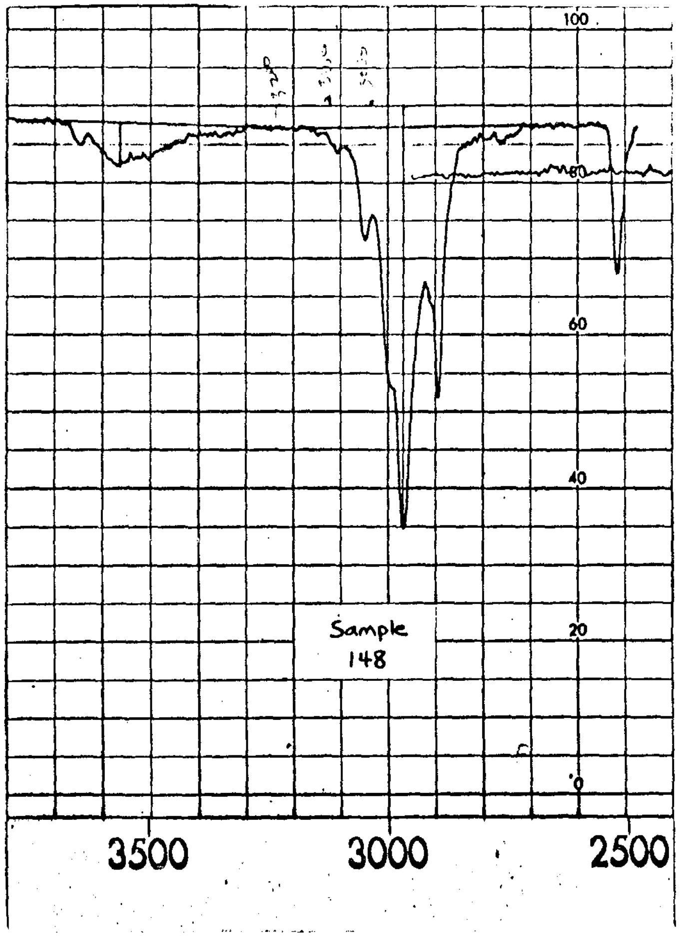
Graph 4i



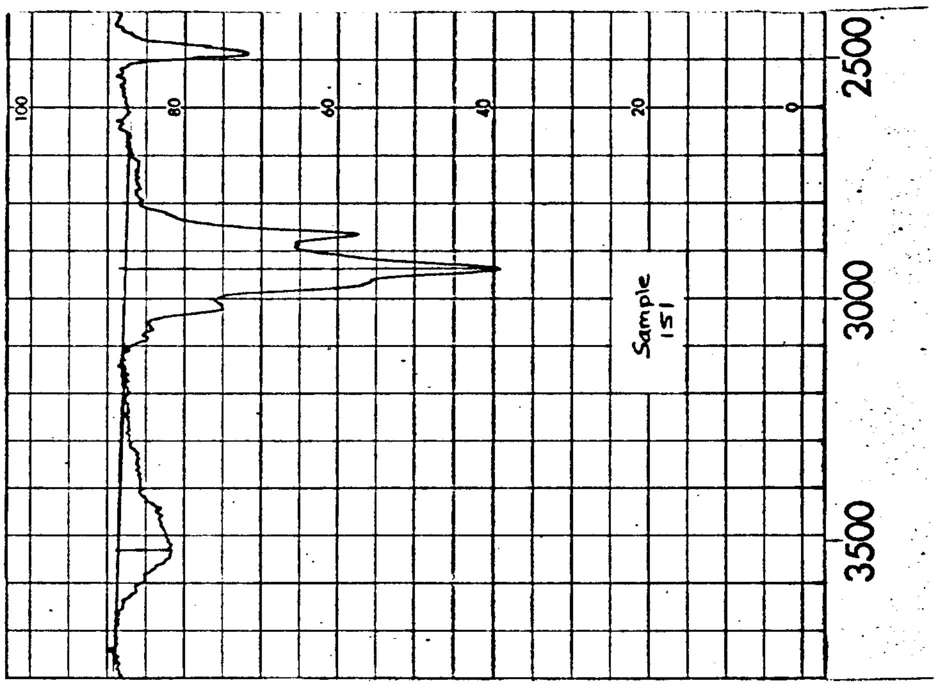
Graph 4 j



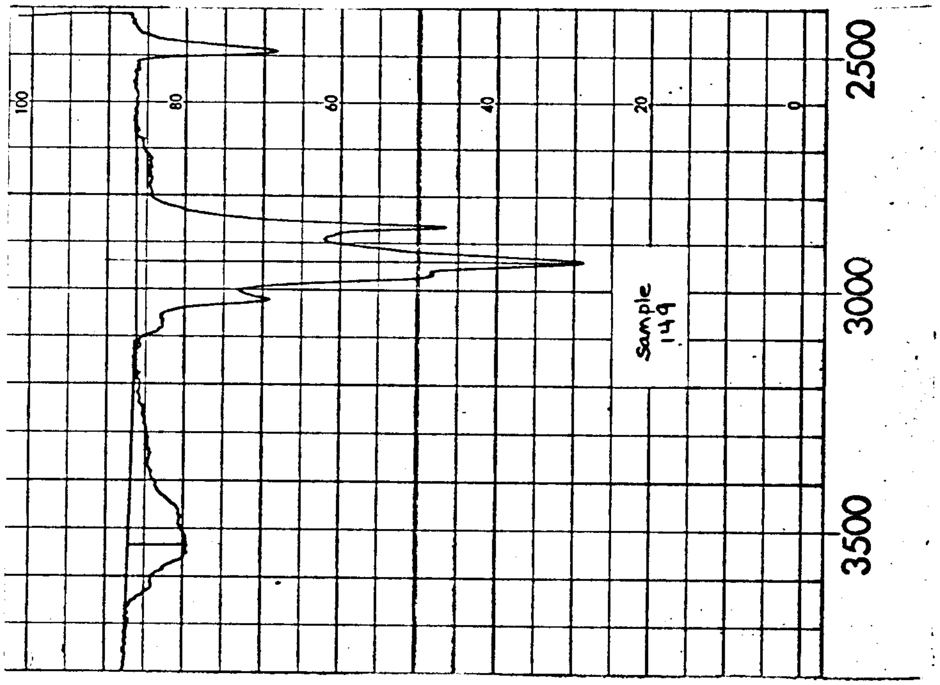
Graph 4k



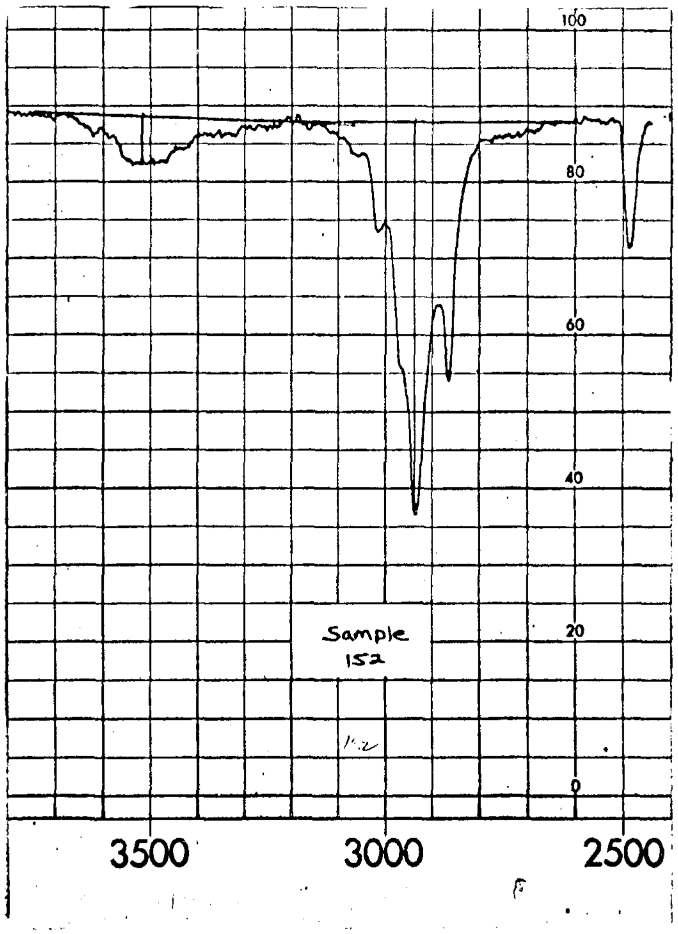
Graph 4l



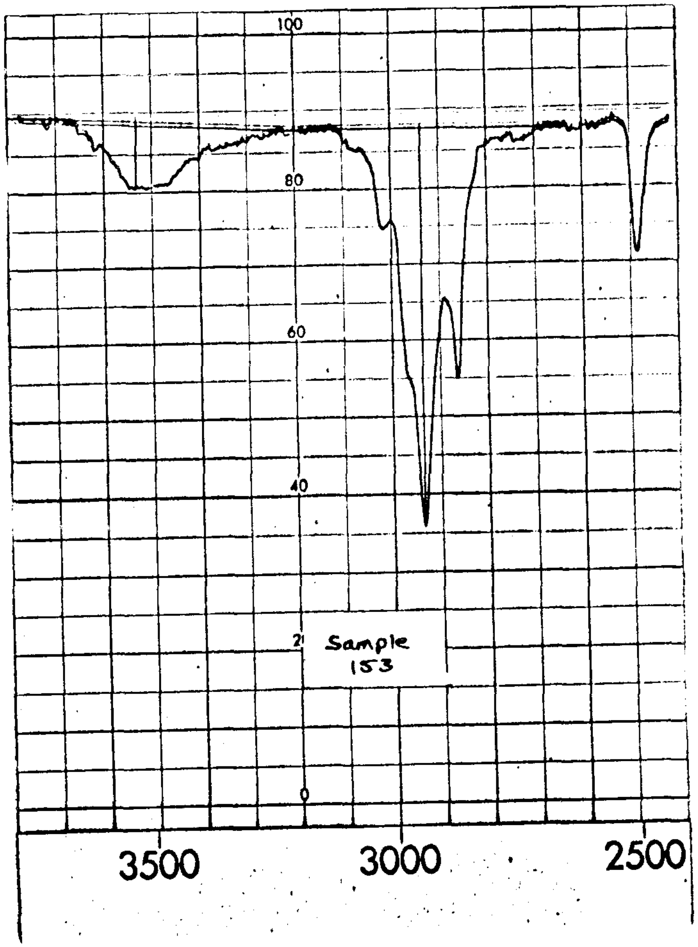
Graph 4n



Graph 4 m



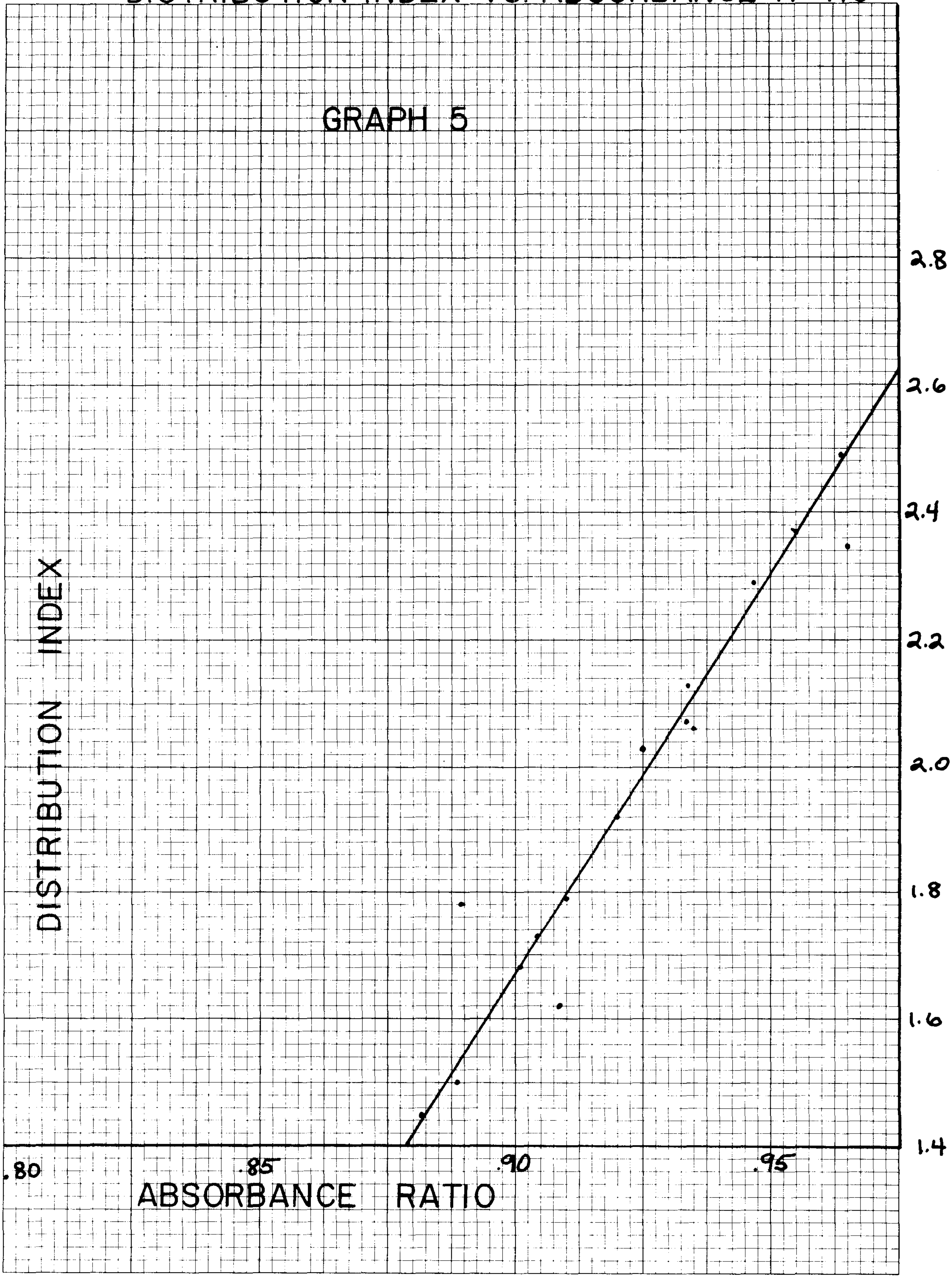
Graph 4o

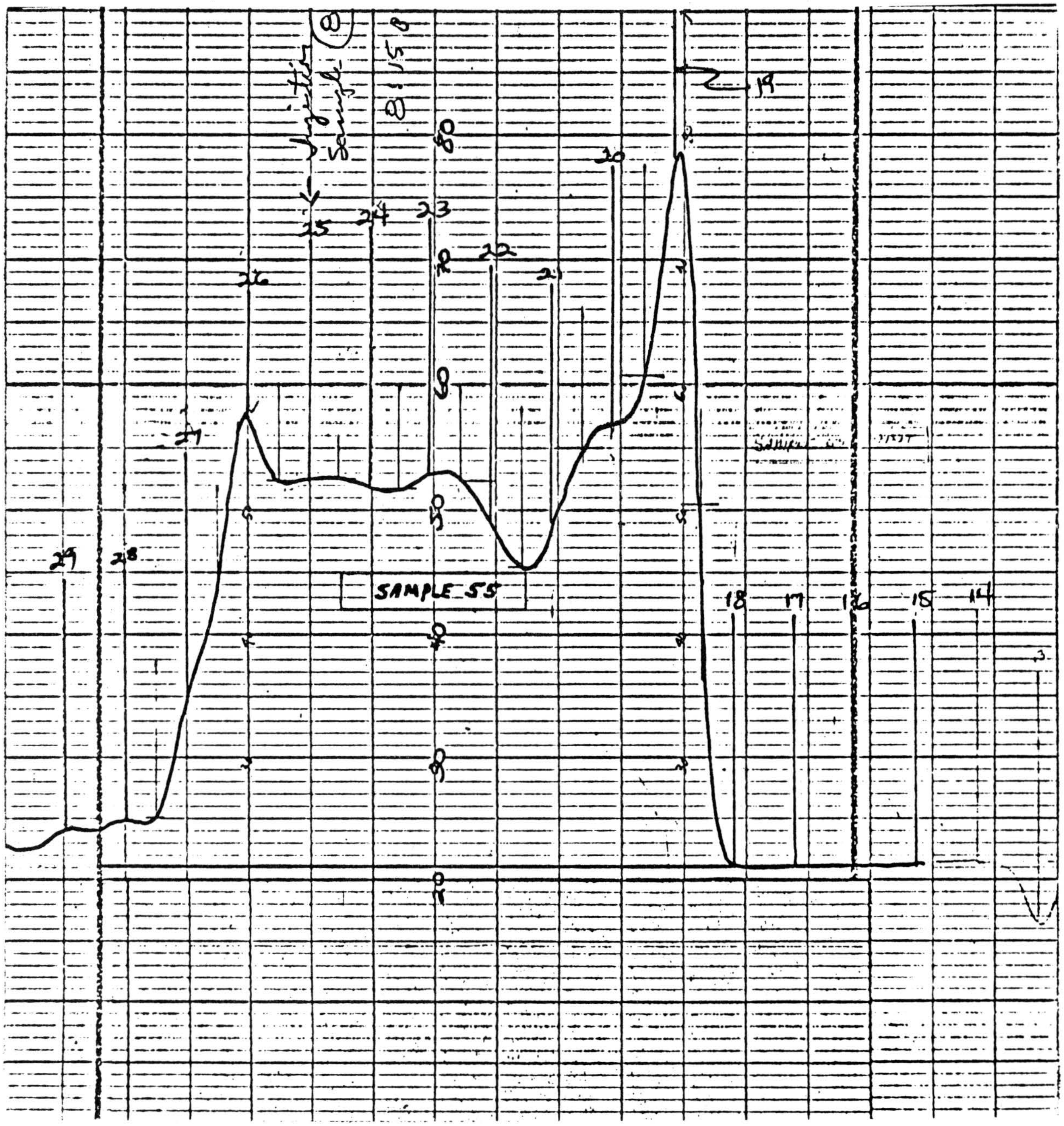


Graph 4p

DISTRIBUTION INDEX VS. ABSORBANCE RATIO

GRAPH 5

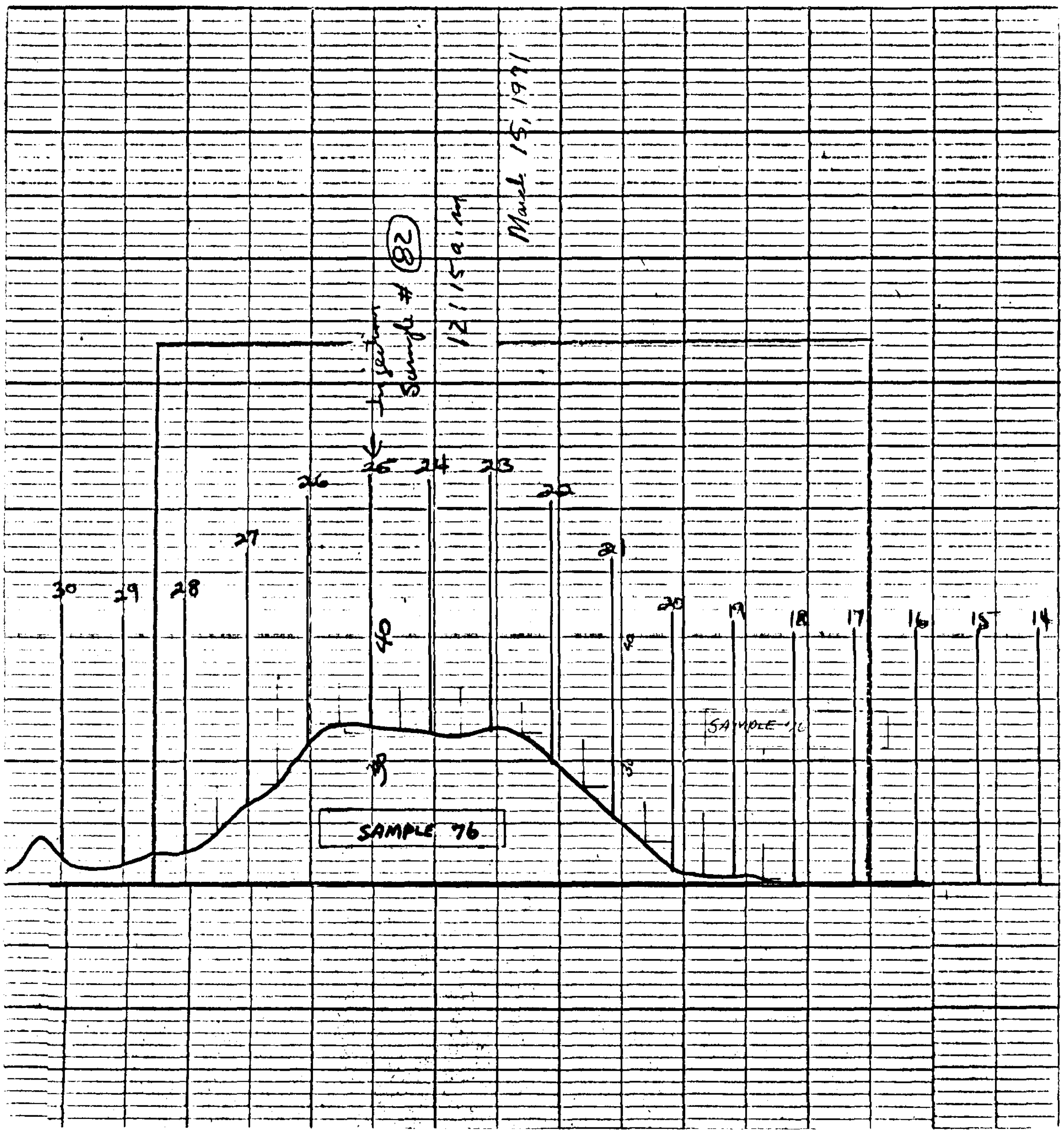




Graph 6a

G.P.C. of Alkyd Resins

Group 1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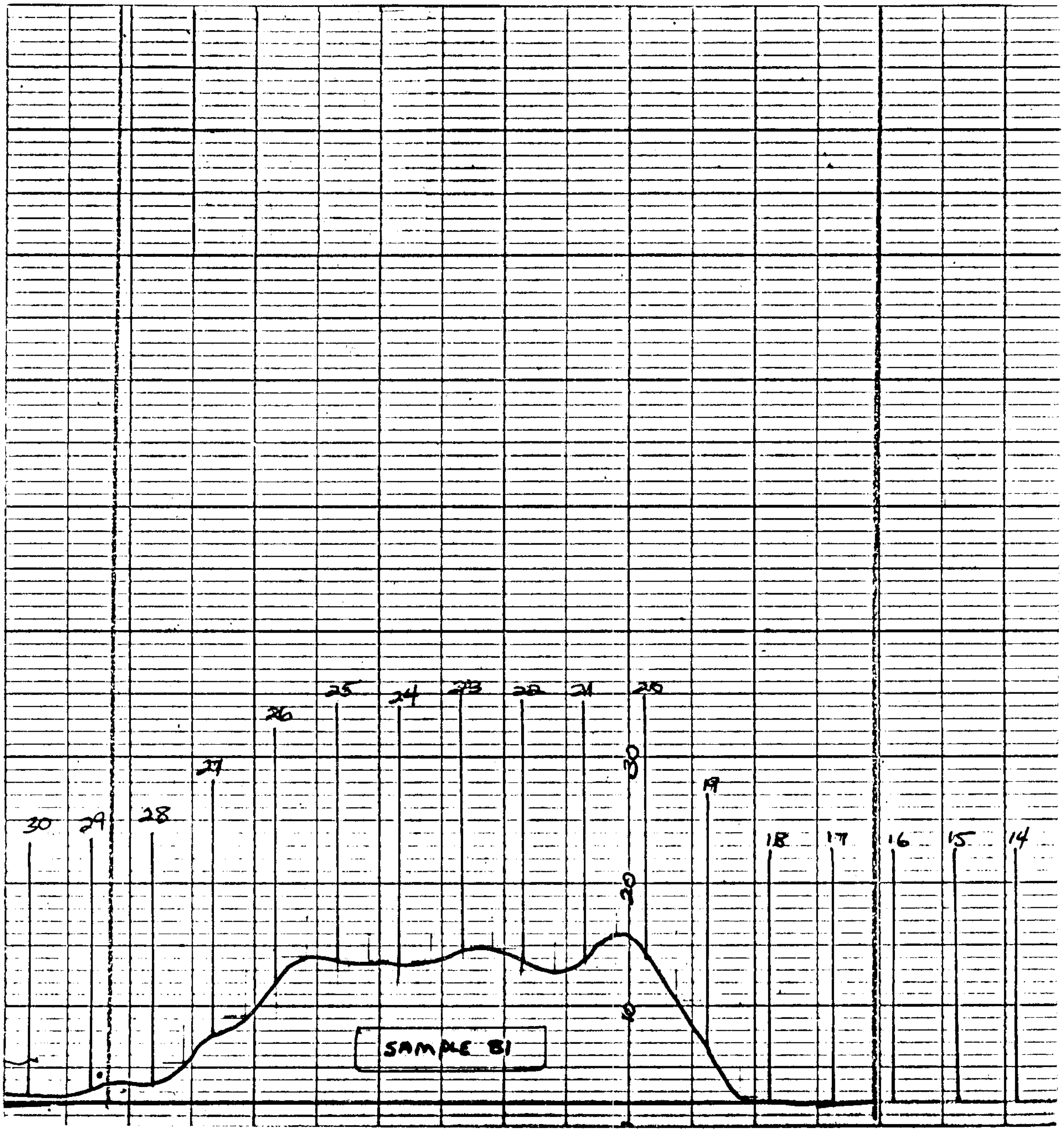
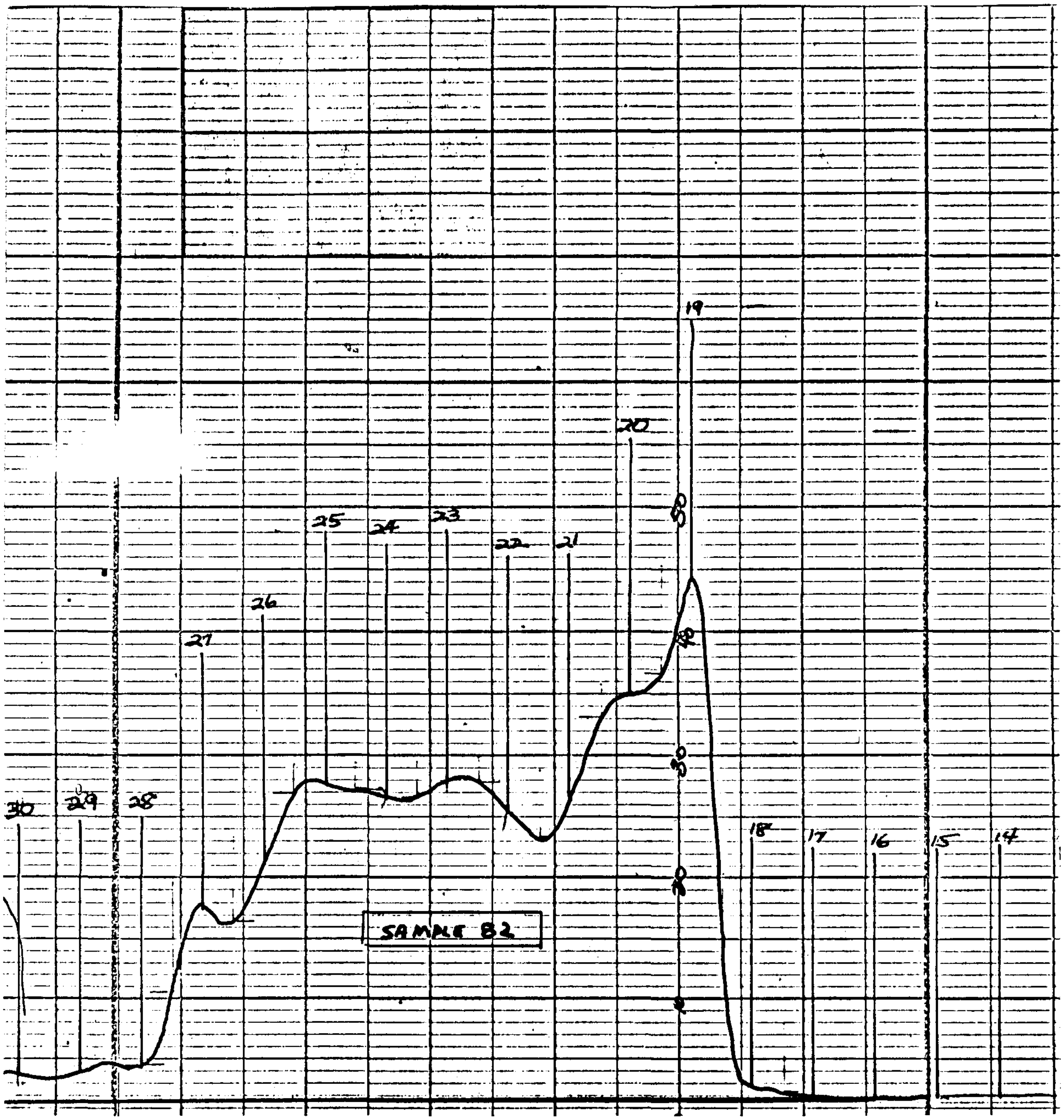
Sample # 82
12:15 a.m.
March 15, 1991
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
40
38
SAMPLE 76

Graph 6b



Graph 6c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27
26
25
24
23
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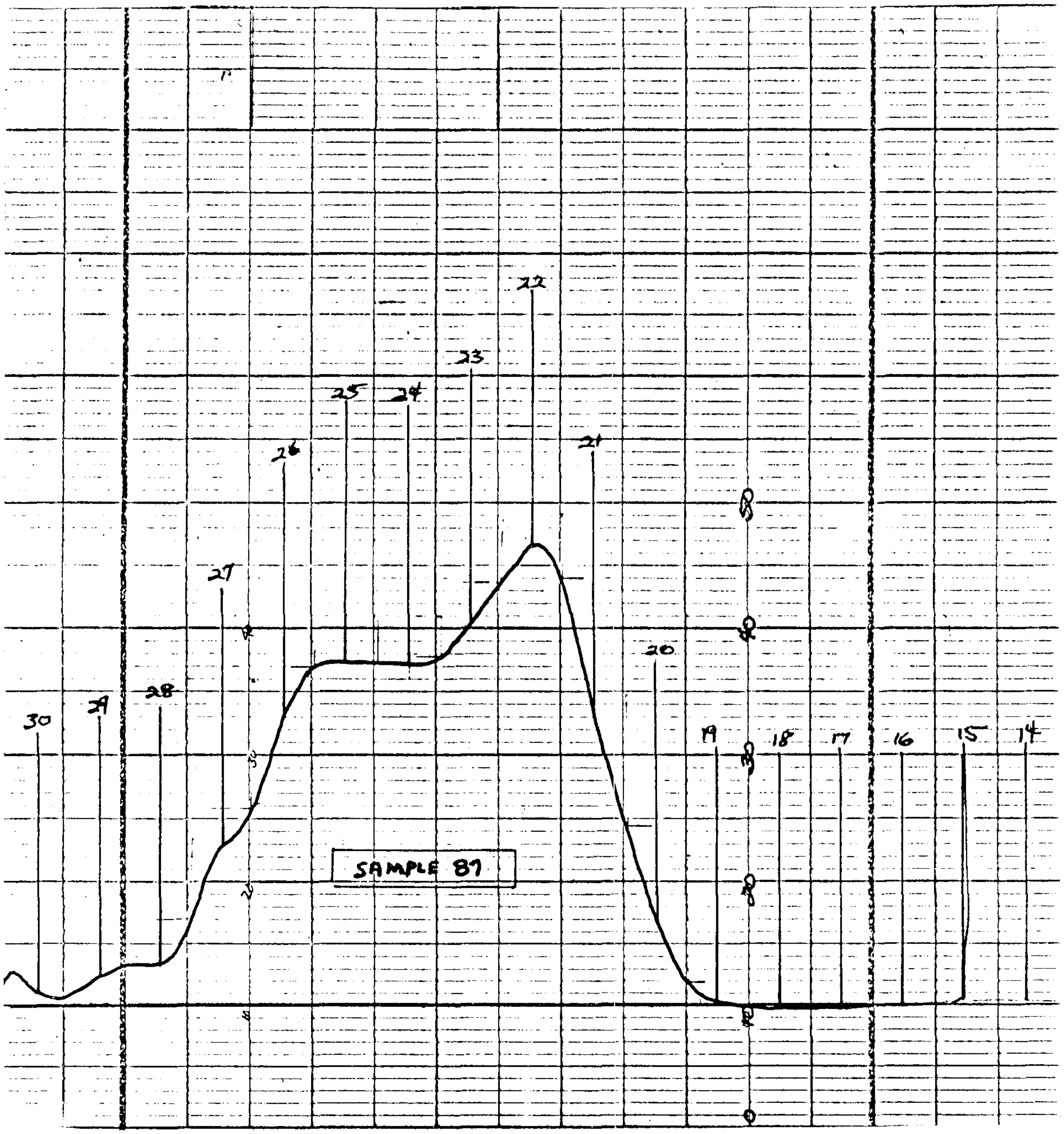
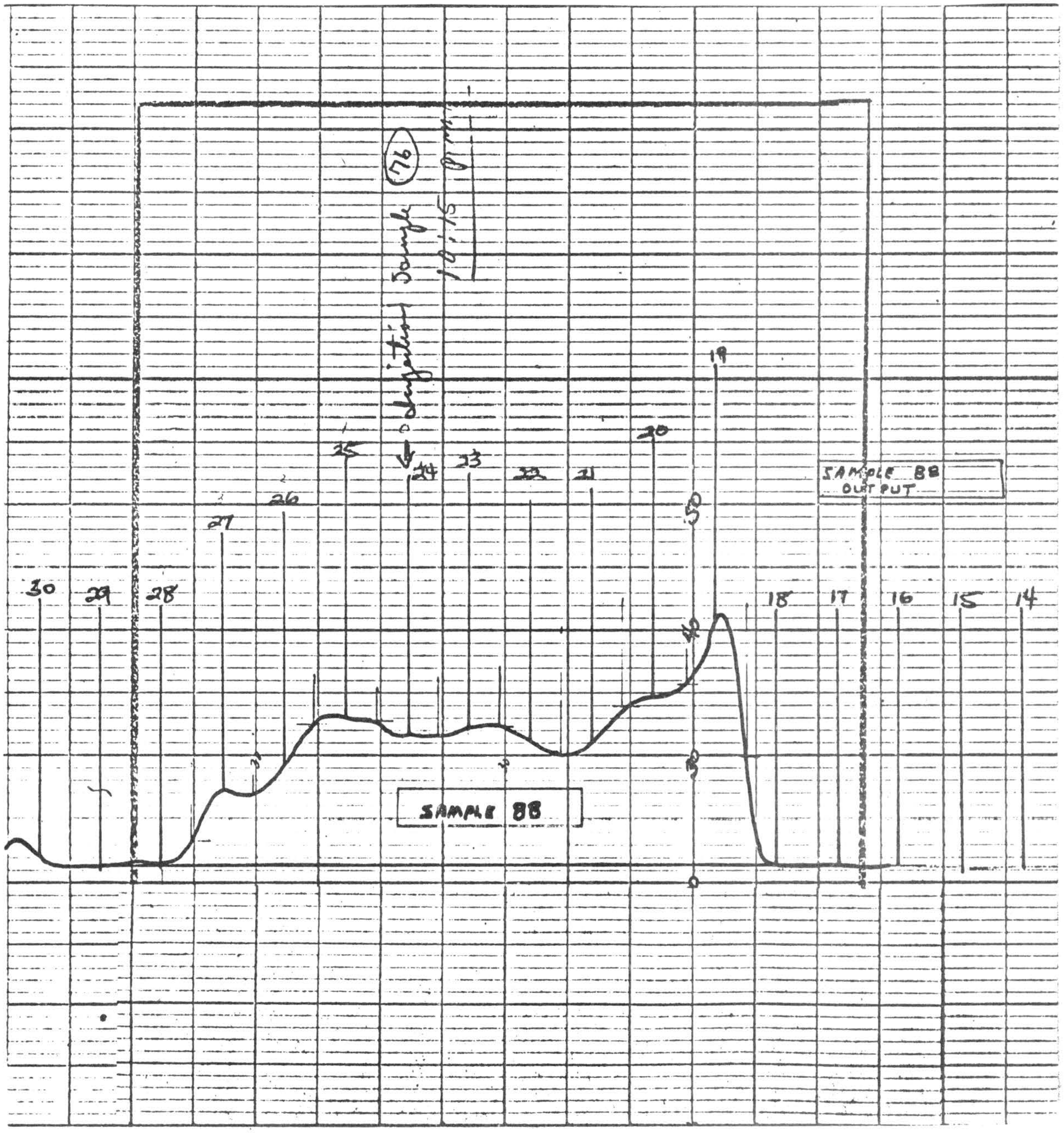
21
20
19
18
17
16
15
14
50
40
30
20
10
SAMPLE B2

Graph 6d



Graph 6e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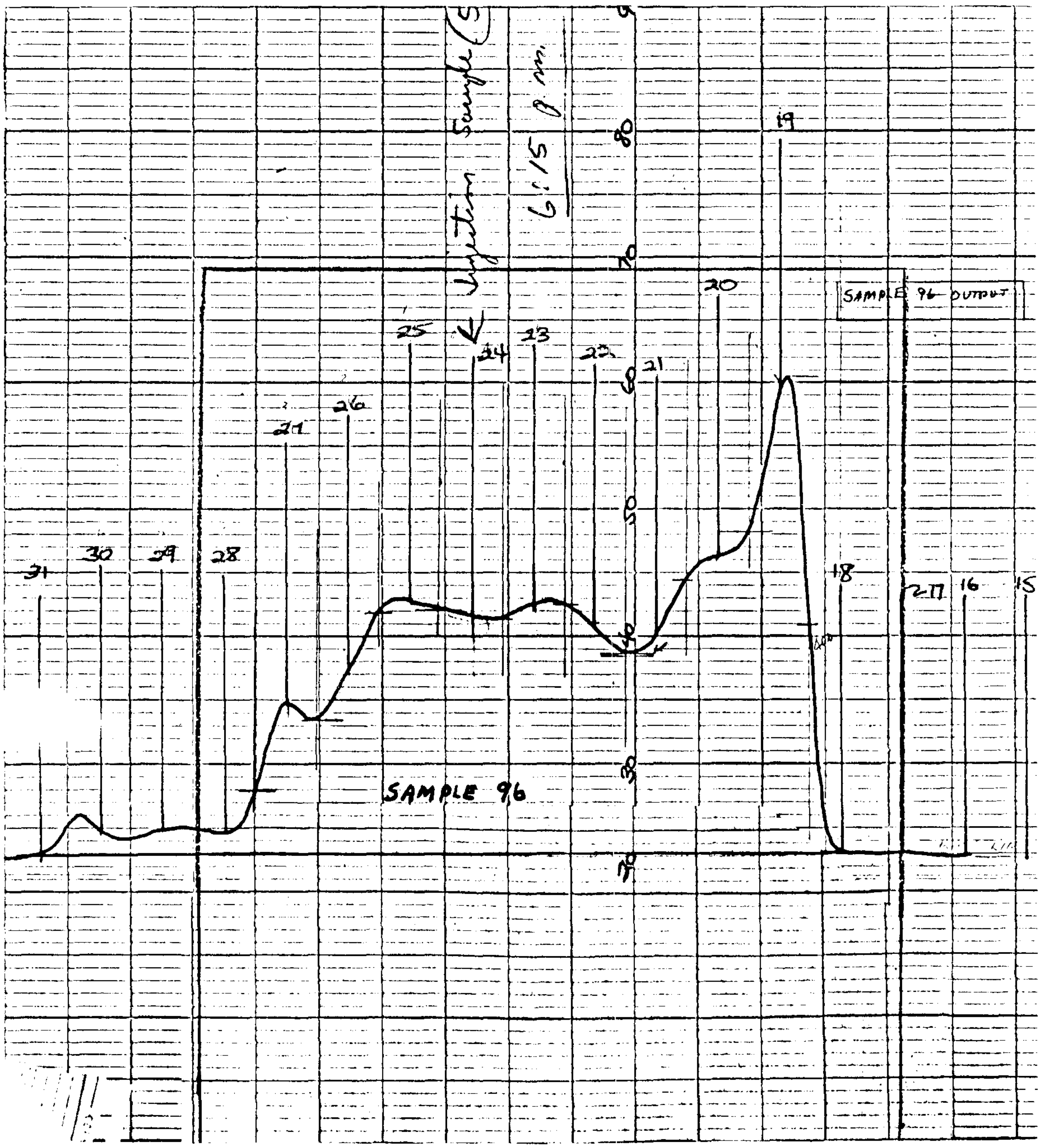
29
28
27
26
25
← Injection Sample (76) 10:15 P.M.
24
23
22
21
20
19
18
17
16
15
14
SAMPLE 88 OUTPUT
SAMPLE 88
50
40
30
0

Graph 6f


Injection Sample (S
6:15 P.M.
SAMPLE 96 OUTPUT
SAMPLE 96
90
80
70
60
50
40
30
20
31
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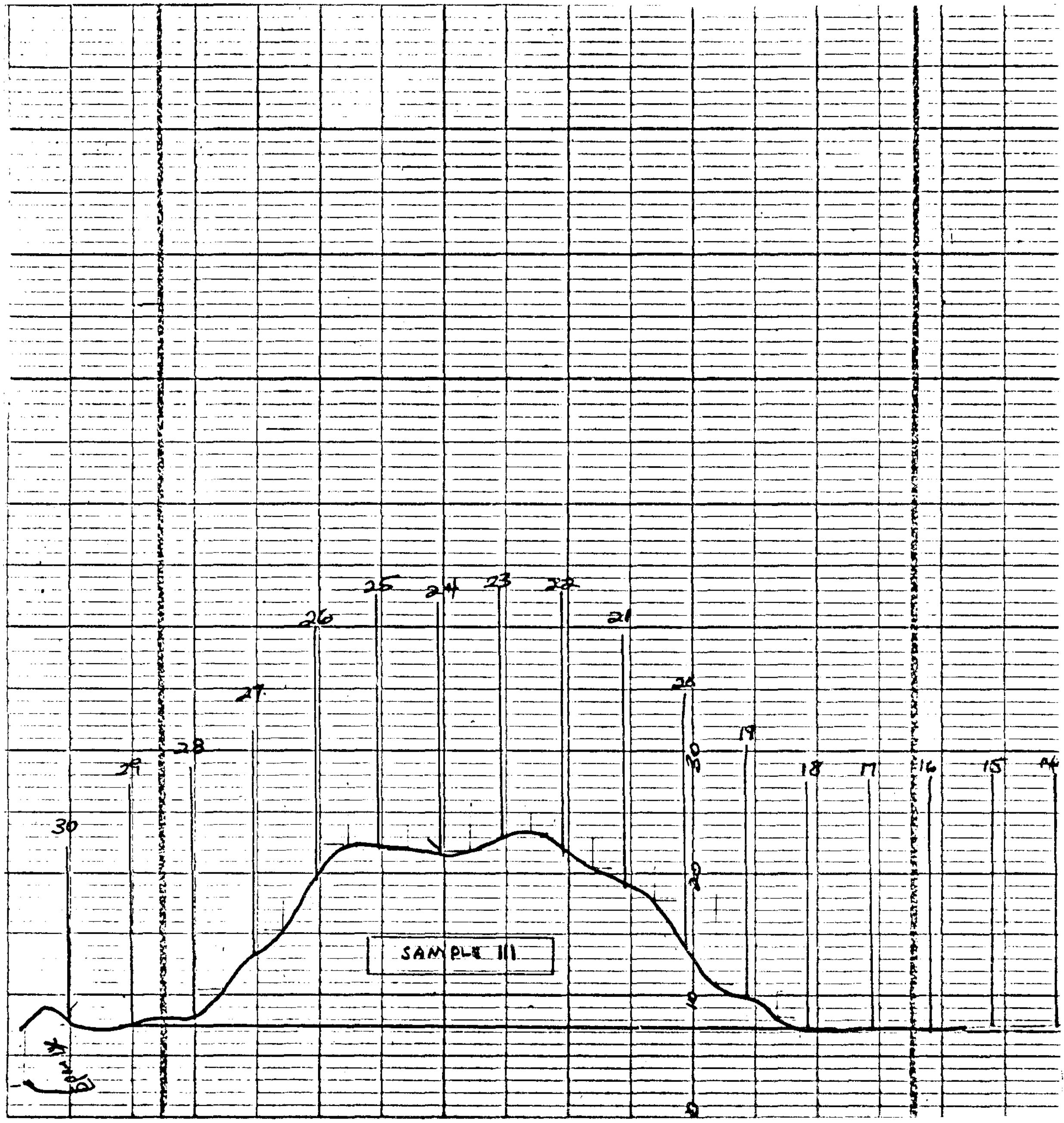
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15

Graph 6g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29
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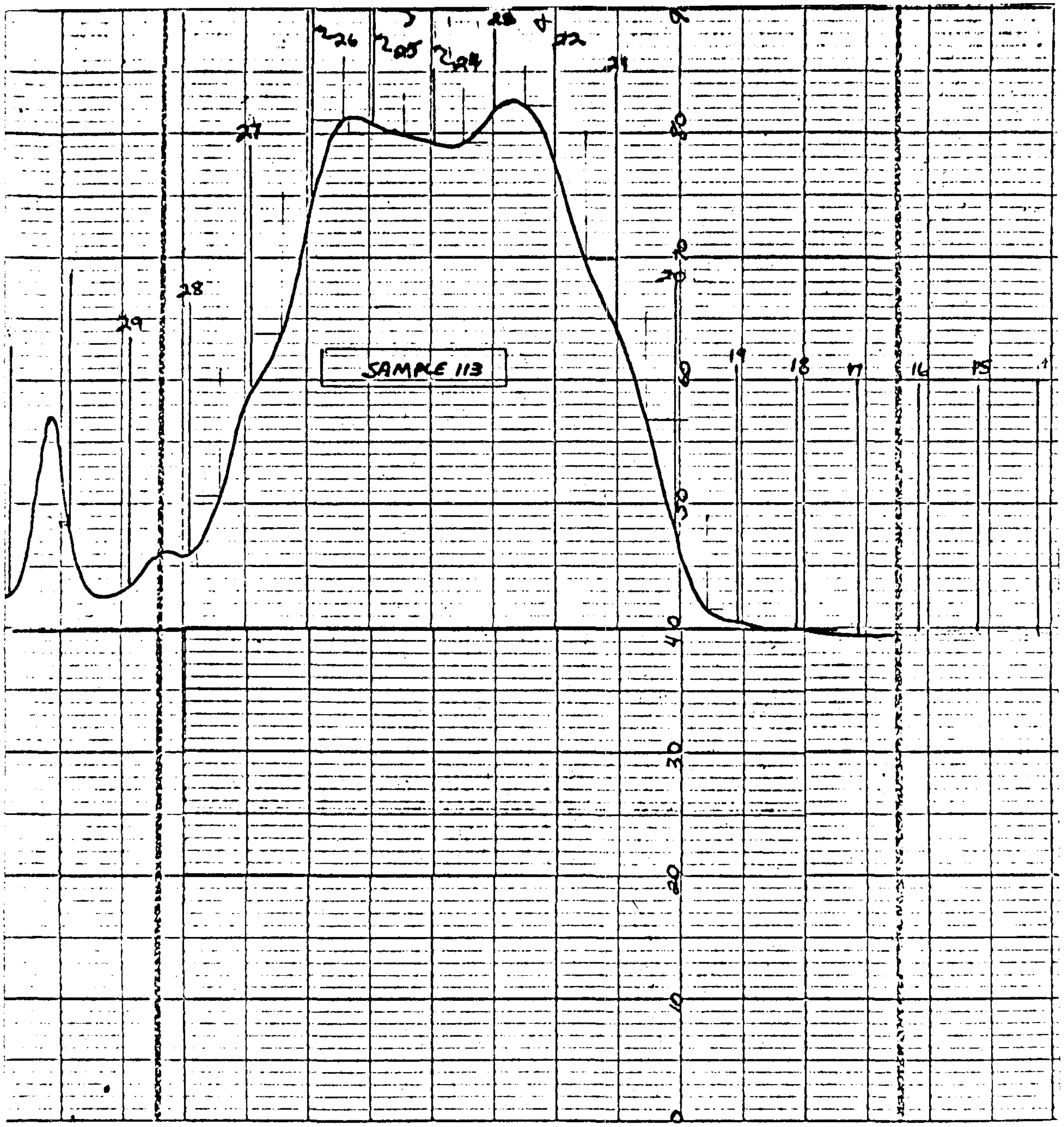
20
19
18
17
16
15
14
30
20
10
0
SAMPLE III
Pool 14

Graph 6h


SAMPLE 113
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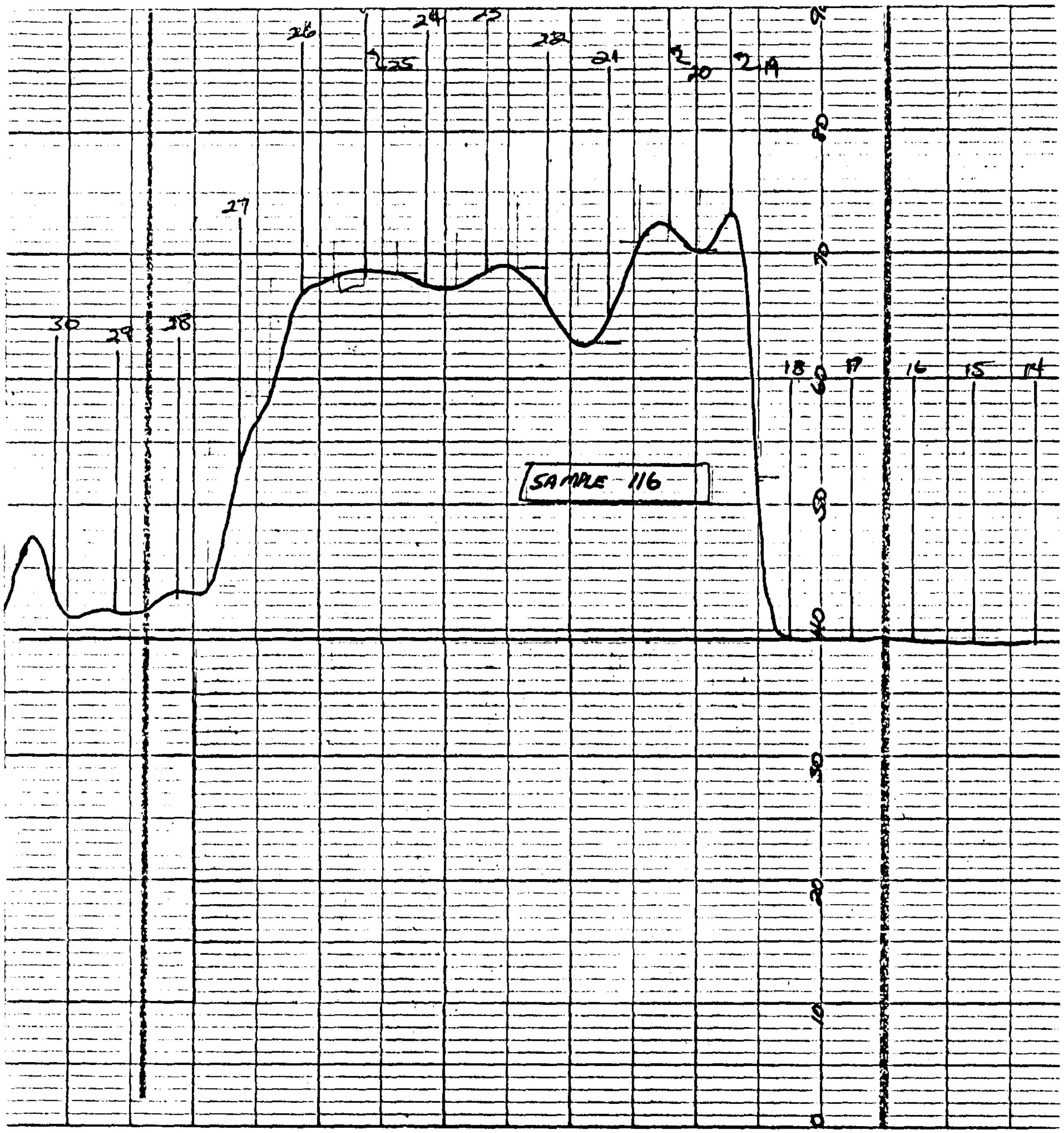
50
40
30
20
10
0

Graph 6i



26
25
24
23
22
21
20
19
27
30
29
28
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16
15
14
SAMPLE 116
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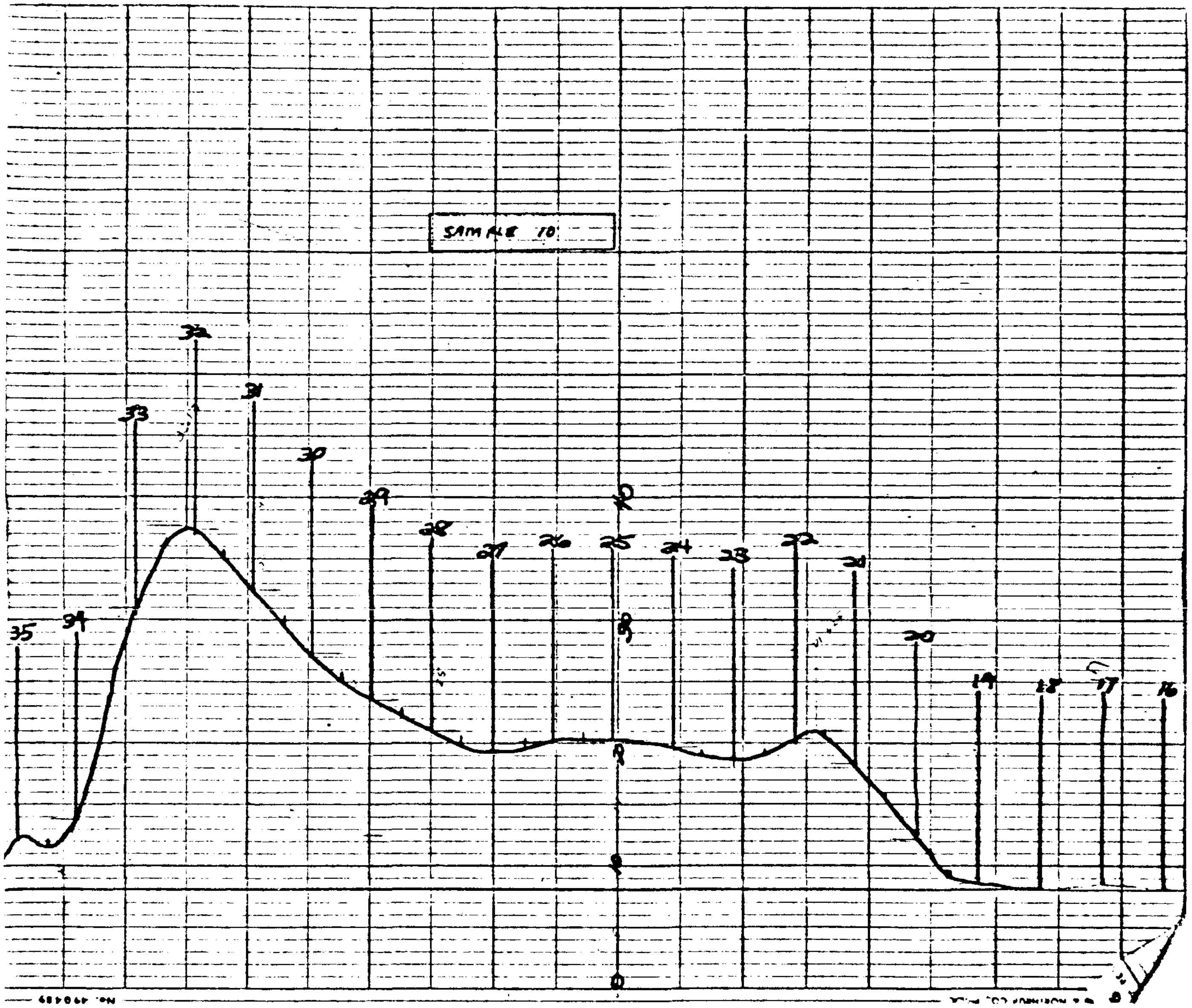
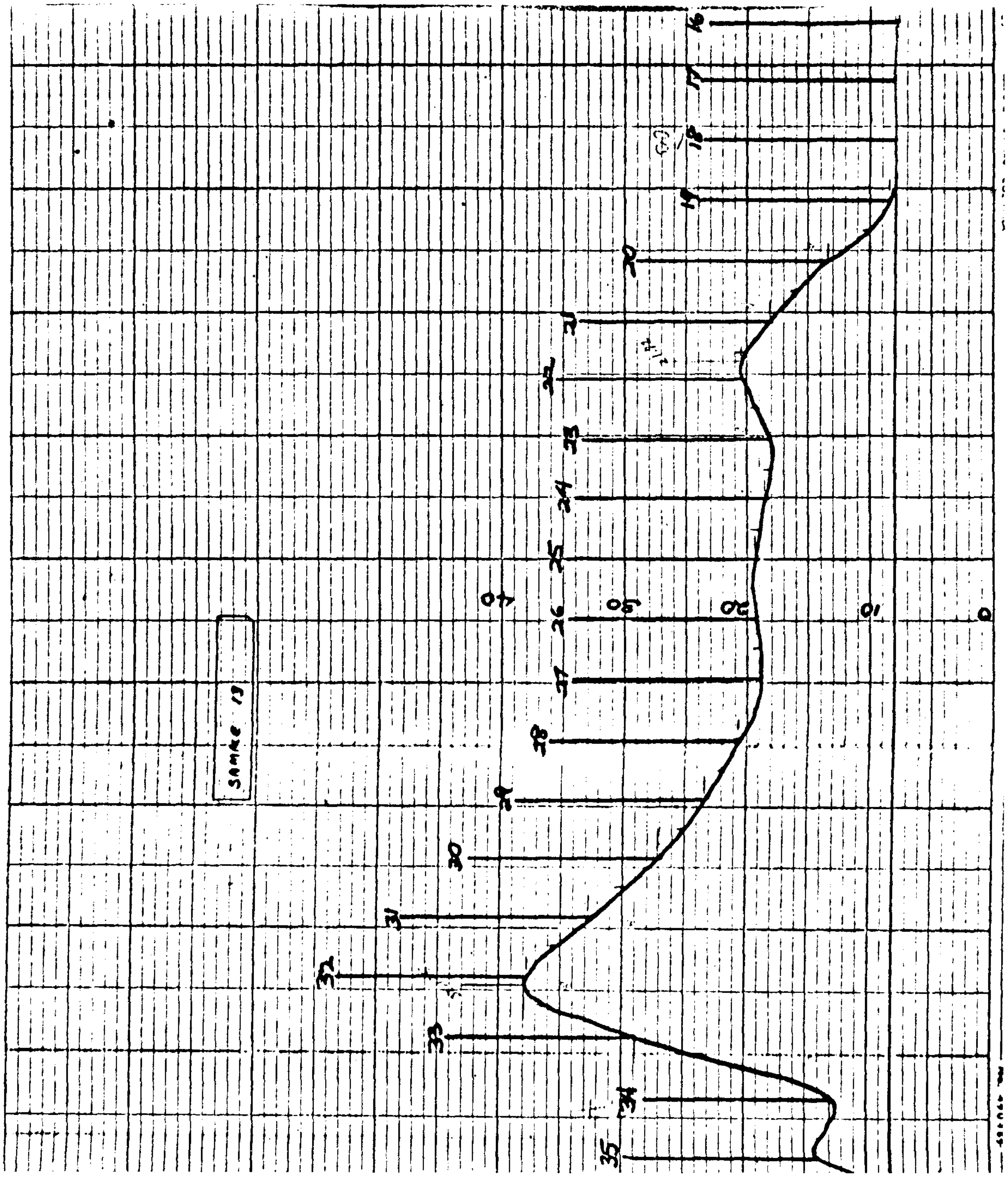
80
70
60
50
40
30
20
10
0

Graph 6j



Graph 7a
G.P.C. of Alkyd Resins
Group 2


SAMPLE 19
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25
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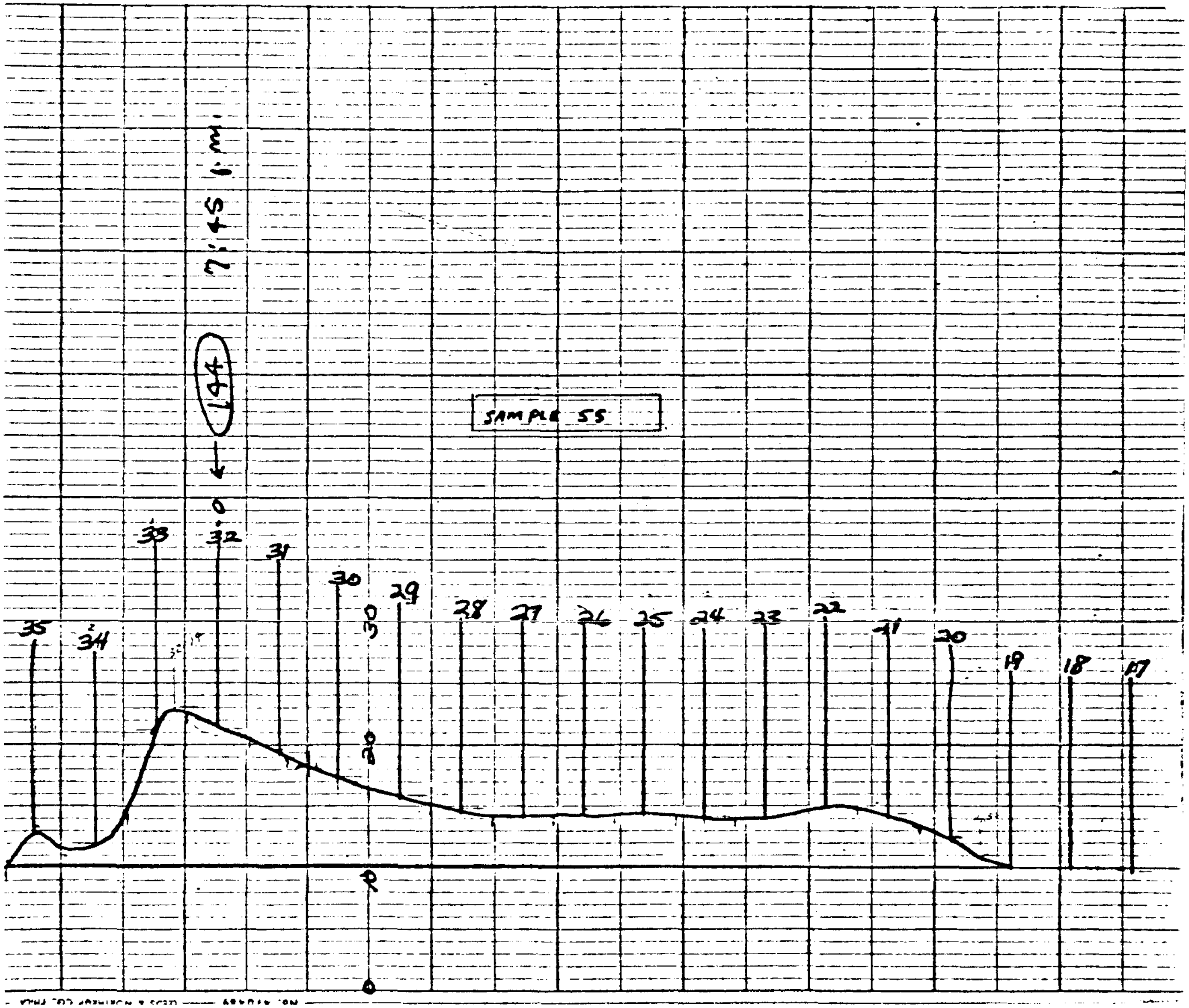
28
29
30
31
32
33
34
35

Graph 7b


7:45 p.m.
194
0
SAMPLE 55
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33
32
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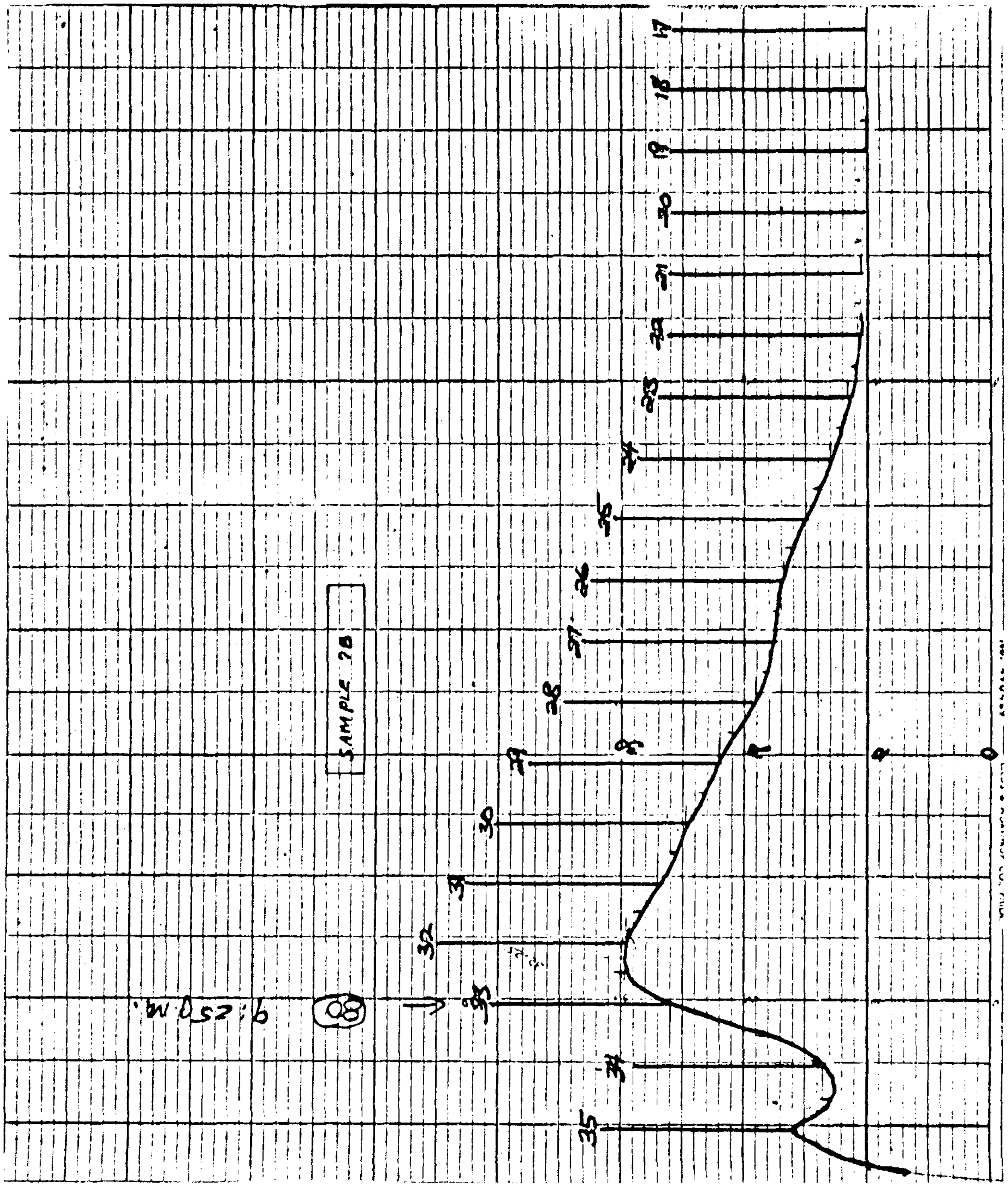
23
22
21
20
19
18
17
30
20
10
0

Graph 7c


SAMPLE 2B
9:25 a.m.
8
35
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33
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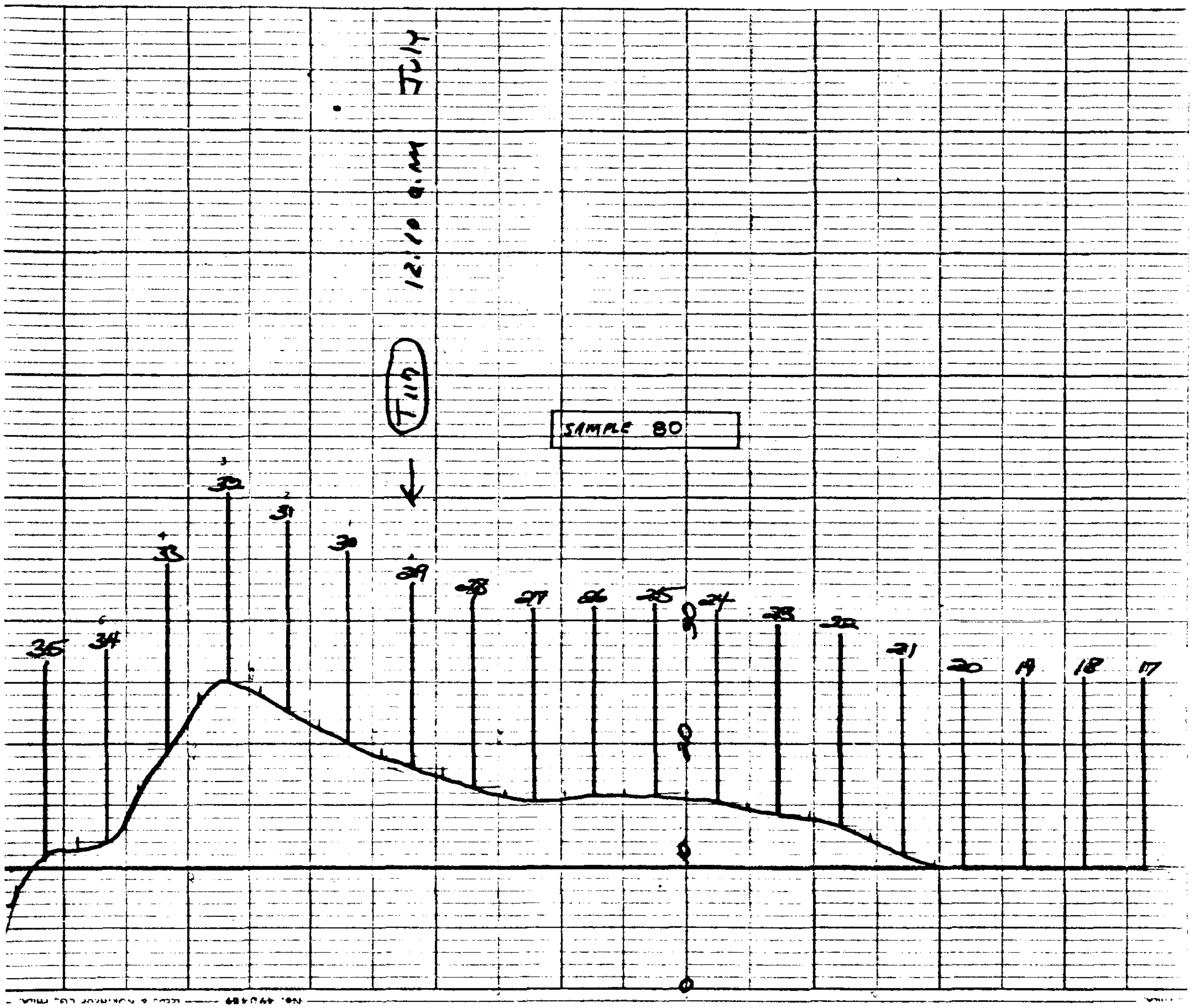
20
19
18
17
R
R
0

Graph 7d


T 119
12:10 a.m.
SAMPLE 80
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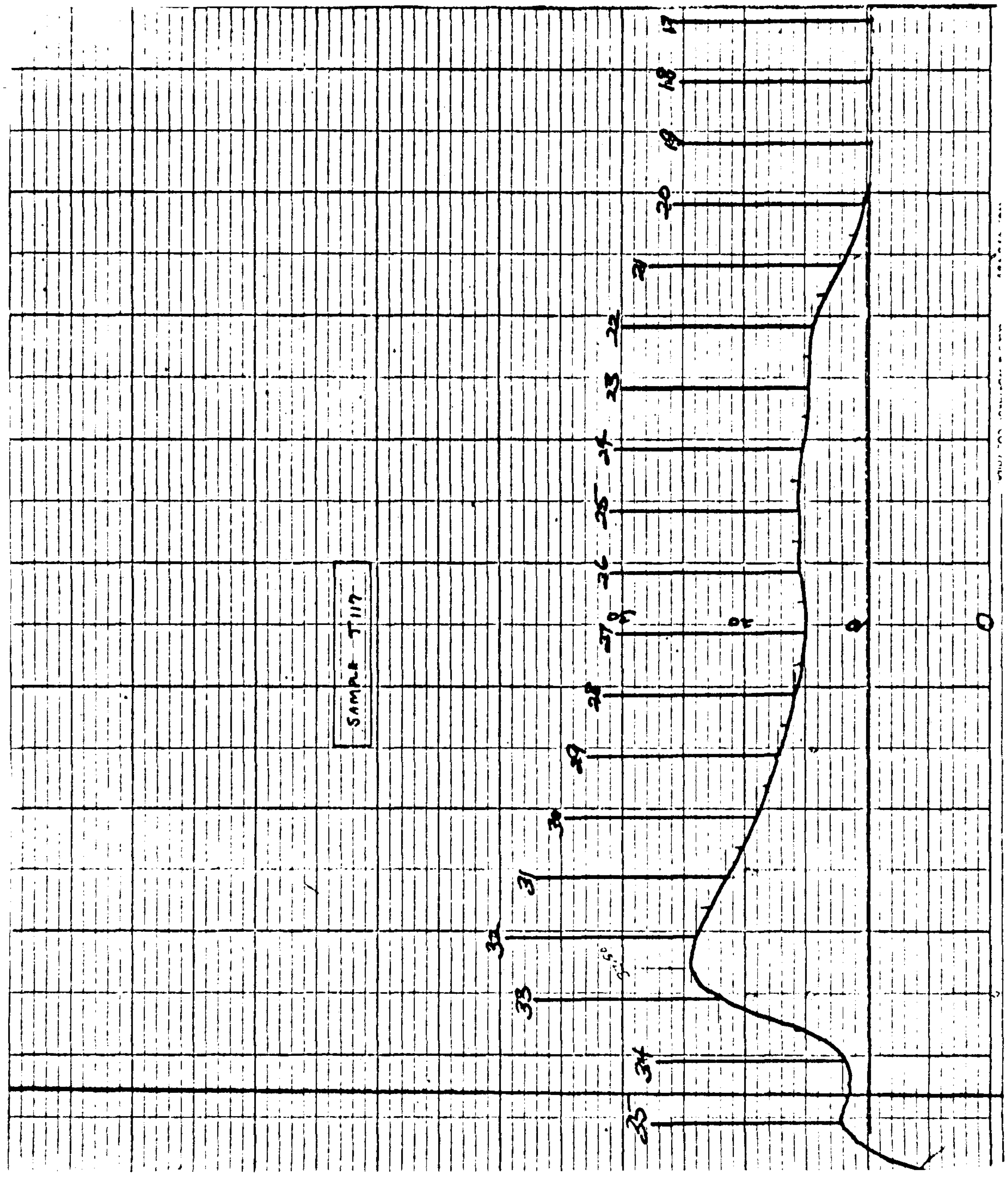
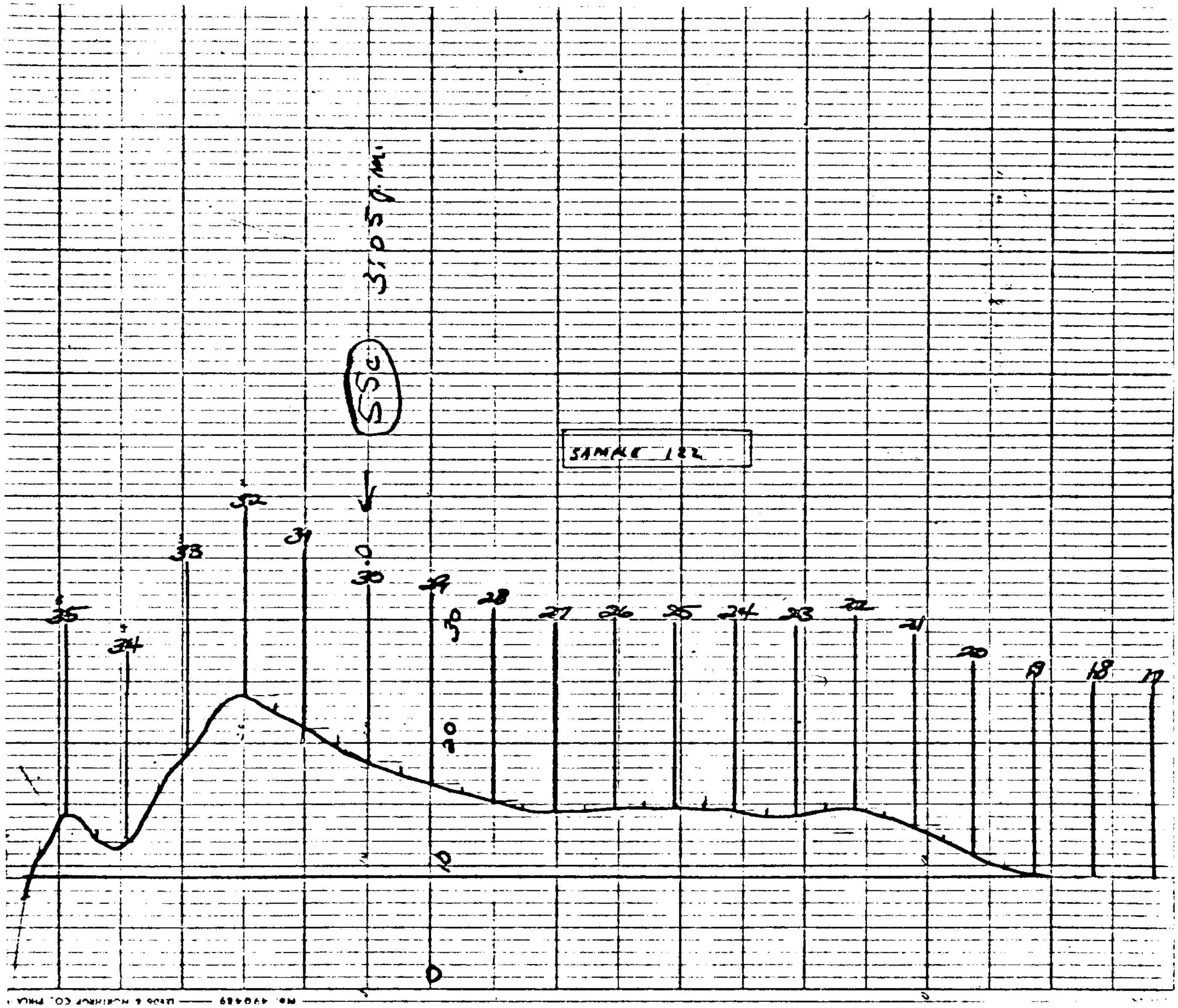
19
18
17
0
0
0

Graph 7e



Graph 7f


3:05 P.M.
SSC
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25
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20
10
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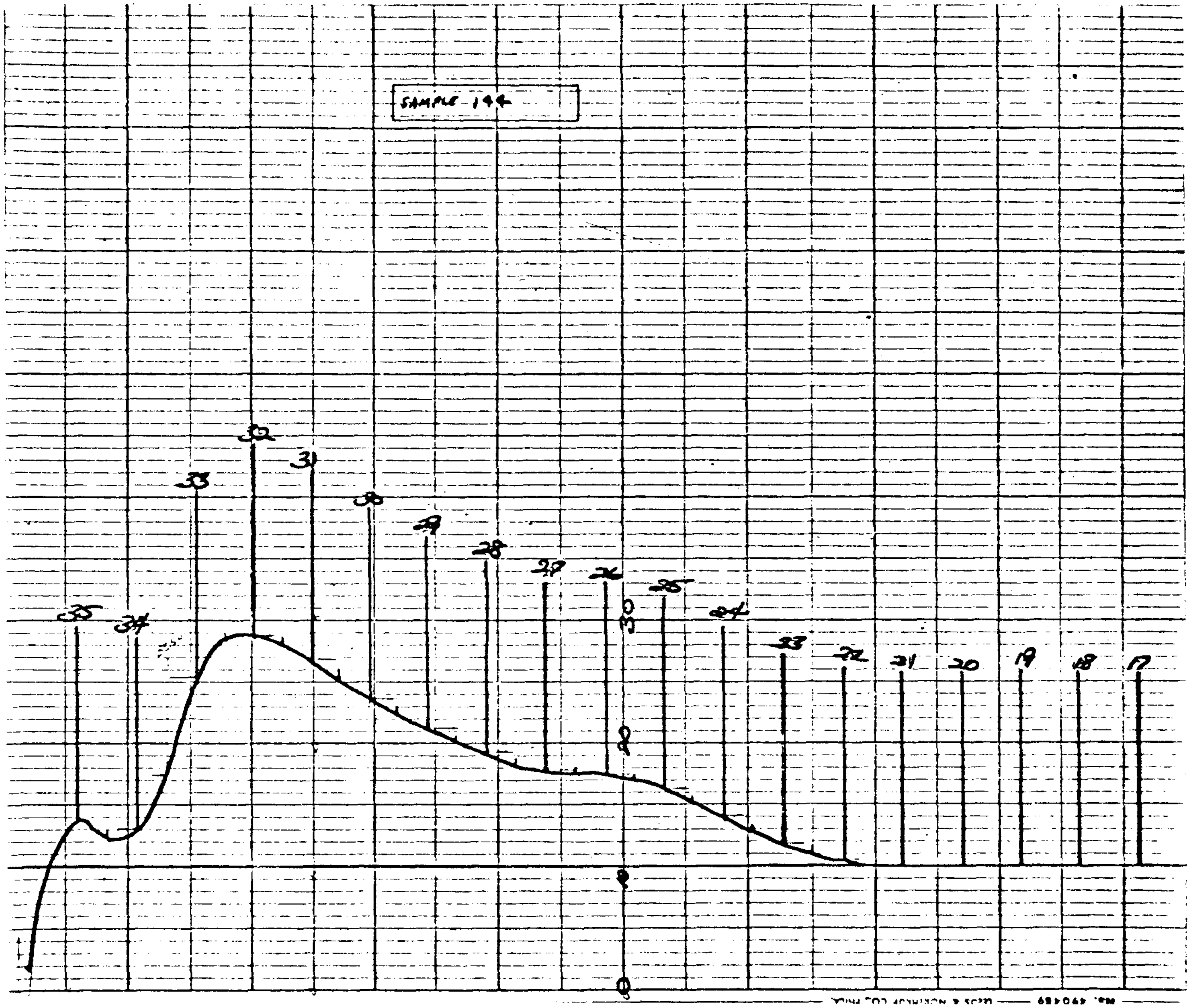
No. 490489 — LEEDS & NORTHRUP CO. PHILA.

Graph 7g


SAMPLE 144
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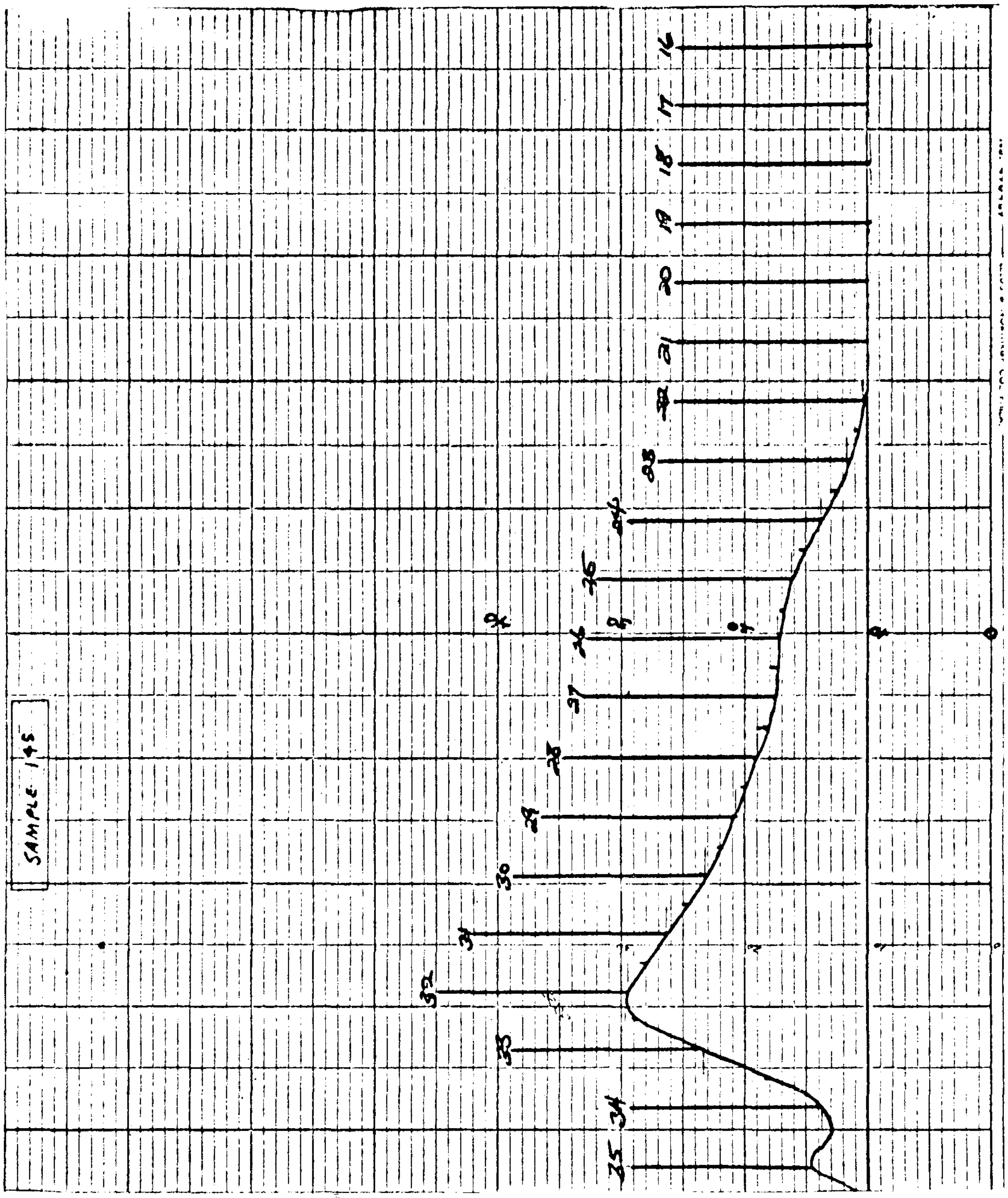
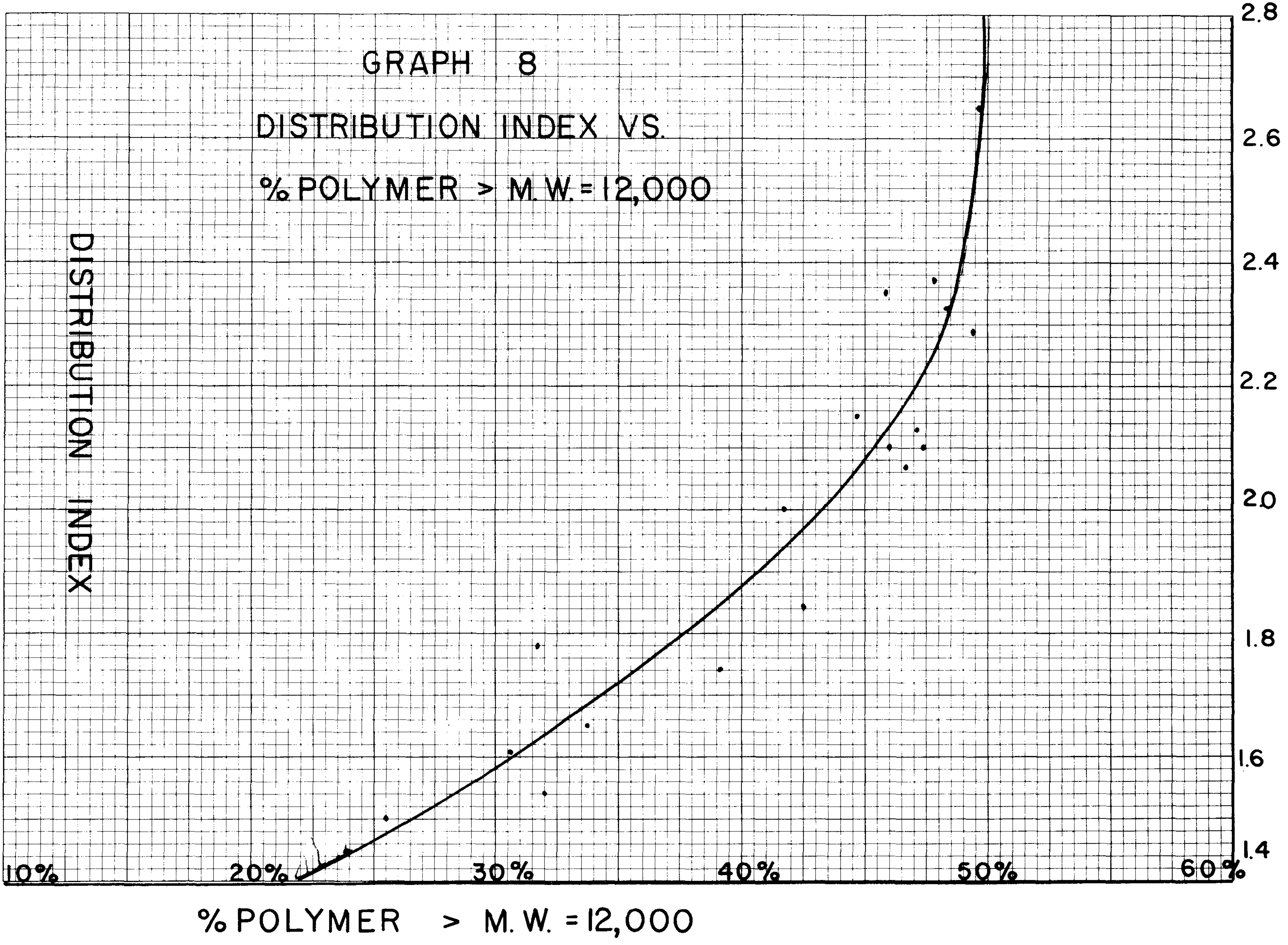
10
0

Graph 7h



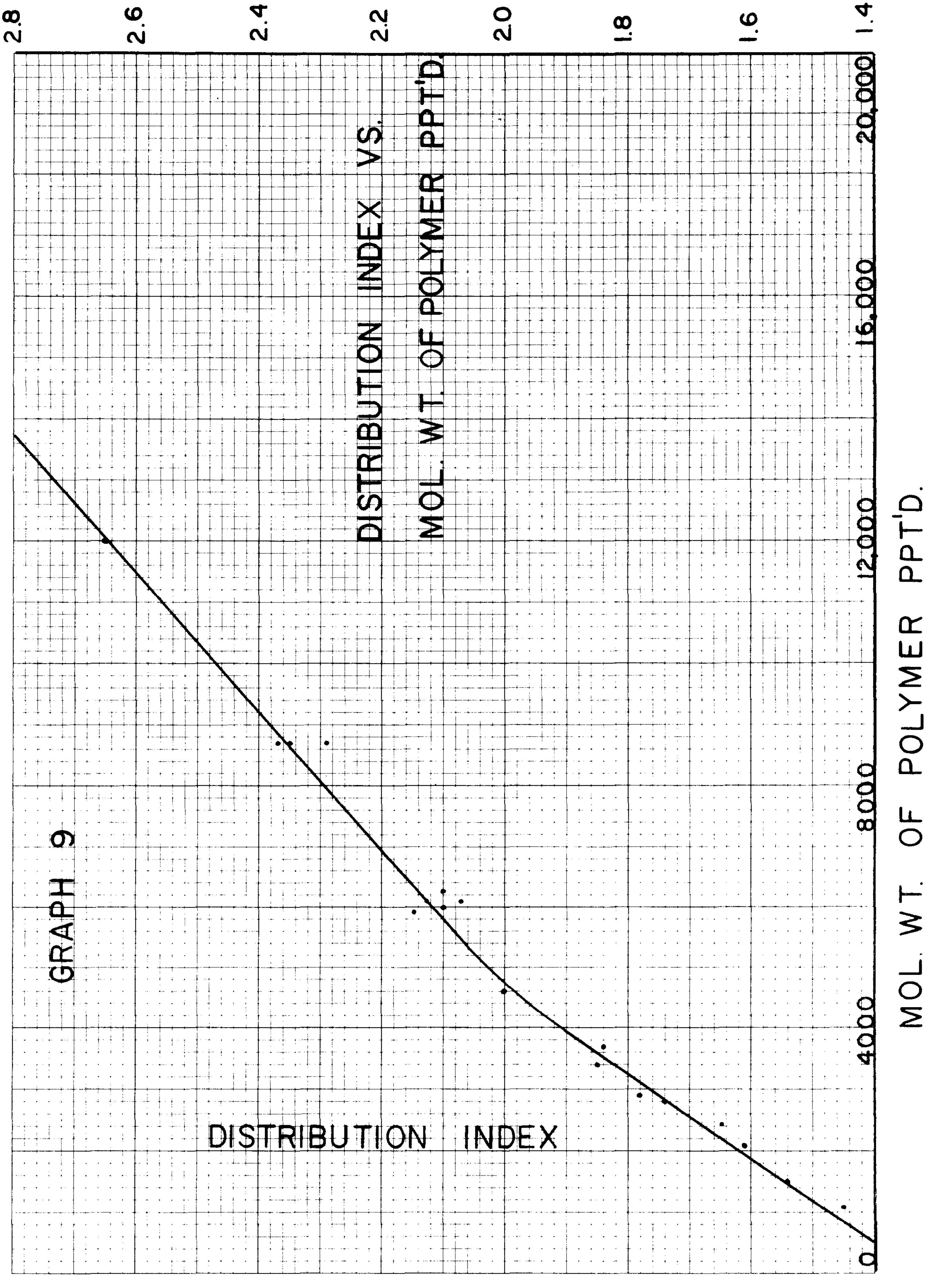
Graph 7i

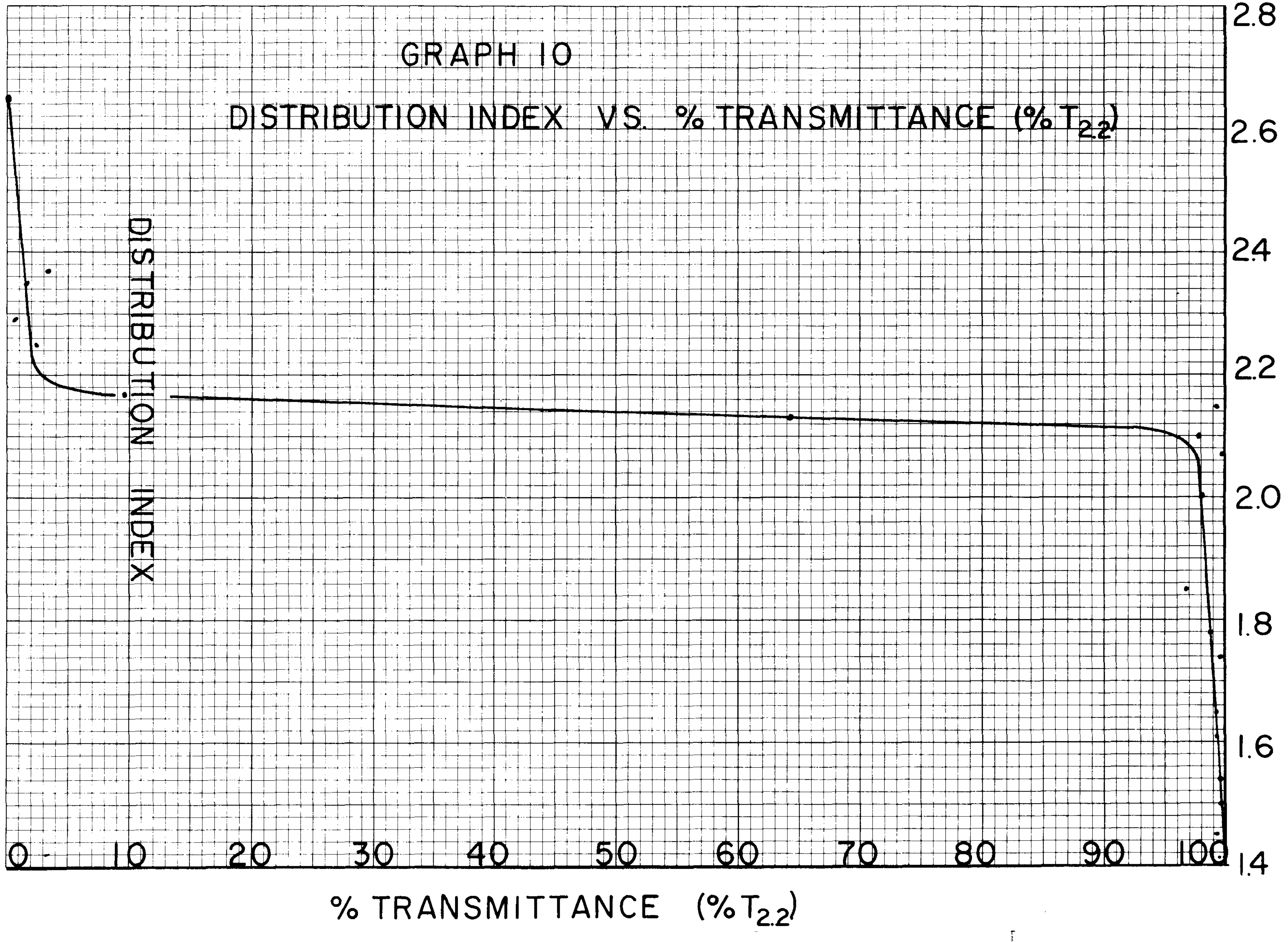


GRAPH 8

DISTRIBUTION INDEX VS.

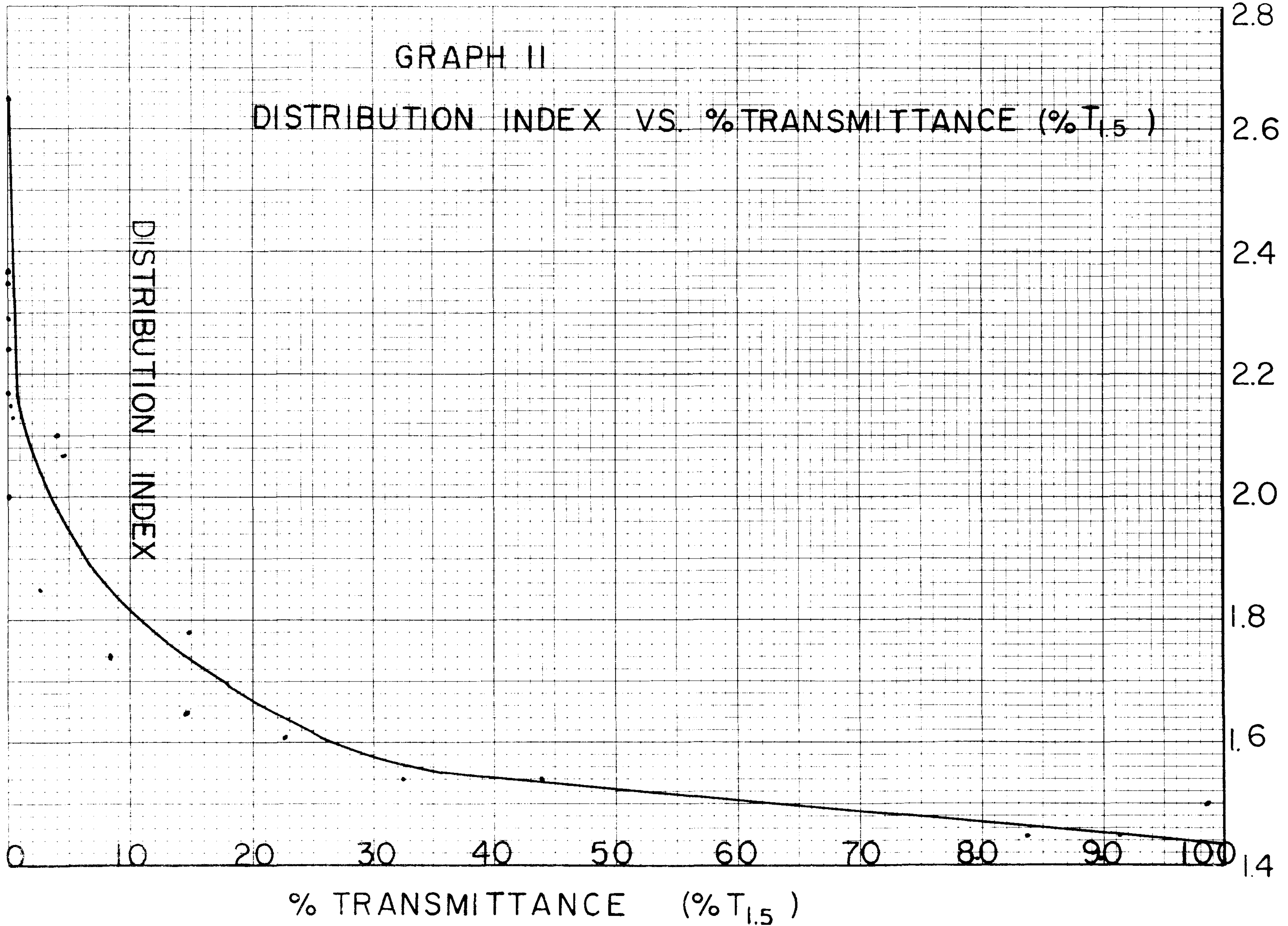
% POLYMER > M.W. = 12,000


GRAPH 9
DISTRIBUTION INDEX VS.
MOL. WT. OF POLYMER PPT'D.
DISTRIBUTION INDEX
MOL. WT. OF POLYMER PPT'D.
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0
4000
8000
12,000
16,000
20,000



GRAPH 10

DISTRIBUTION INDEX VS. % TRANSMITTANCE (%$T_{2.2}$)



GRAPH II

DISTRIBUTION INDEX VS. % TRANSMITTANCE (%$T_{1.5}$)

Test Method Tex-   -B
Tentative

Texas Highway Department

Materials and Tests Division

METHOD FOR THE DETERMINATION OF MOLECULAR CHARACTERISTICS OF COATING RESINS BY TURBIDIMETRIC MEASUREMENT

Scope

This method describes the apparatus and procedure required to determine molecular characteristics of coating resins by turbidimetric measurement.

Apparatus

1. Beckman Model DK-2A Dual recording spectrophotometer or other ultraviolet visible spectrophotometer having comparable sensitivity and accuracy at the specified wavelength.
2. 10 mm pyrex absorption cell.
3. 250 ml wide-mouth Erlenmeyer flask
4. 100 ml Geissler buret with 0.2 ml subdivisions.
5. A primary solvent as specified in the resin specification.
6. A precipitating agent as specified in the resin specification.
7. Magnetic stirrer and 1-inch stirring bar.
8. 6" x 6" x 1/8" asbestos sheet.

Procedure

1. Prepare a solvent mixture as outlined in the resin specification.
2. Weigh by difference from a syringe or other suitable container, sufficient resin solution to yield 0.4 - 0.6 grams of resin

solids. Transfer the sample into the sample flask. Place an asbestos sheet on top of the magnetic stirrer and position the sample flask on top of the asbestos sheet. Immediately start the magnetic stirrer. (Note: The sample solution is to be maintained at an ambient temperature of 25° ± 1°C and continuously stirred throughout the turbidimetric analysis.)

3. To the sample flask deliver the required amount of solvent mixture as specified in the resin specification. The sample is to be kept under continuous agitation and the rate of solvent addition should be adjusted to maintain uniform dispersion of the resin sample in the solvent.

   Upon the completion of the addition of solvent mixture, the sample flask is sealed with a stopper and allowed to stir for 5 minutes prior to transmittance measurement.

4. The ultraviolet visible spectrophotometer is adjusted to meet the following conditions:
   - a. Energy level - single beam
   - b. Wavelength setting = 750 mμ
   - c. Sensitivity control setting = 50
   - d. Slit opening = 0.10 mm
   - e. Cell (pyrex) = 10 mm pathlength

Standardize the instrument in the following manner:

a. Set the pen to record 0% Transmittance with the sample shutter "closed".

b. Set the pen to record 100% Transmittance when the 10 mm absorption cell filled with the primary solvent (as specified in the resin specification) is placed in the sample beam and the sample shutter is in the "open" position. (Note: The spectrophotometer should be standardized prior to each turbidimetric measurement.)

5. After the required 5 minute agitation period, a sample of approximately 4 ml is extracted from the sample flask and delivered into the 10 mm absorption cell. The cell is positioned in the spectrophotometer and the % Transmittance is recorded. The absorption cell is then removed from the spectrophotometer and the sample solution returned to the sample flask.

6. To the sample solution, add the calculated amount of precipitating agent, as specified. The rate of precipitating agent addition should be adjusted such that developing turbidity occurs only briefly in the vortex produced by the stirring bar. The concentration of precipitating agent should not be allowed to accumulate in an isolated area of the flask. In addition, the rate of agitation may require necessary adjustment to insure uniform

dispersion of the resin sample in the solution. Upon completing the addition of precipitating agent, the sample flask is stoppered and agitation is continued for 5 minutes.

7. Repeat the standardization procedure (Step 4).

8. At the end of the second 5 minute agitation period, approximately 4 ml of the sample solution is removed from the flask and delivered into the 10 mm absorption cell.

9. The % Transmittance is recorded for the sample solution containing precipitating agent.

   Report the results in the following manner:

   a. % Transmittance of resin sample after addition of solvent mixture = % T_1.

   b. % Transmittance of resin sample after addition of solvent mixture and precipitating agent = % T_2.