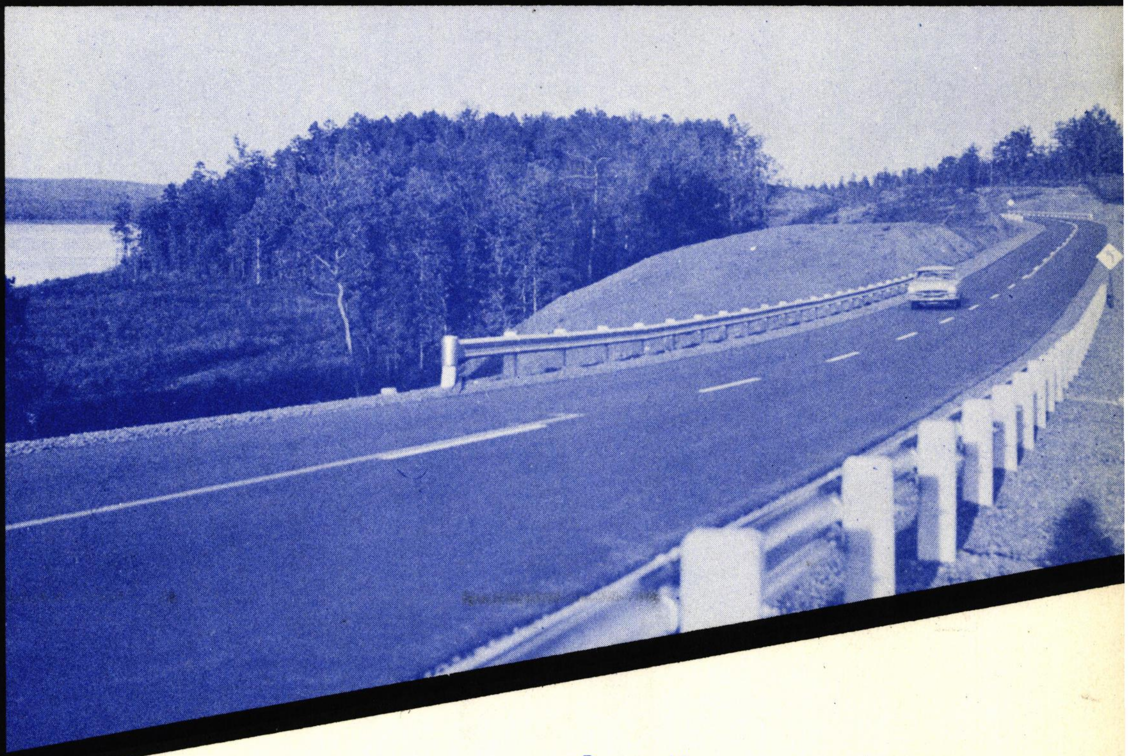
J. Clements

correlation of physical properties with chemical composition of paving grade asphalts

FINAL REPORT

HRC #21 - RHEOLOGY OF ASPHALT CEMENTS



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in cooperation with the
U. S. Department of Transportation
Federal Highway Administration
for the
Arkansas State Highway Department
Division of Planning and Research

december 1972

R & D IMPLEMENTATION DATA SHEET

PART A

REPORTING STATE ARKANSAS

NOTE - The receiving office will code card Col. 3 thru 7, and 17 thru 25.

1 2	3	4 6	7	8	9 16	17 23	24	25	26 31	32 37	38 43
State	Yr	Id. Num.	UD	Cd	State Project Number	FCP Code	A P	Fnd	Proj. Start Date Mo. Day Yr.	Proj.Compl. Date Mo. Day Yr.	Date This Report Mo. Day Yr.
0 3				A	2 1 K 4 5 7		2	1	0 7 0 1 6 4	0 9 3 1 7 1	1 2 3 1 7 2

44 47
STUDY COST To Date ($1000's)
1 0 6

PART B

48	49	50	51	52	53	54
IS	IO	IP	IA	TA	RU	NI
2	2				2	3

IMPLEMENTATION STATUS = (IS) in Col. 48
1 Implemented (ing) - Code Col. 49 & 52
[✓ 2] Implementable - Code Col. 49, 50, & 51
3 No implementation planned - Code Col. 53 or 54

IMPLEMENTABLE BY OTHERS = (IO) in Col. 49
1 By most other states
[✓ 2] Some other states
3 No other states
4 Other (Explain)

IMPLEMENTATION PLANS = (IP) in Col. 50
1 Will be implemented or underway in next 12 months
2 Will be implemented or underway in next 24 months
3 Implementation is planned, subject to action noted, in Col. 51

IMPLEMENTATION ACTION NEEDED = (IA) in Col. 51
1 Equipment changes or modifications needed
2 Administrative decision required
3 Need new or revised procedures, guidelines, manual, &/or standards or specifications
4 Training aids need to be prepared
5 Other (Explain)

NOT IMPLEMENTABLE = (NI) in Col. 54
1 Negative findings
2 Confirms present practice
[✓ 3] Additional evaluation or study needed
4 Findings too complex
5 " impractical
6 " inconclusive
7 " unreliable
8 Other (Explain)

RESULTS POTENTIALLY USEFUL = (RU) in Col. 53
1 A phase, or one of a group of studies
[✓ 2] Points up need for further research
3 Findings are theoretical in nature
4 Exploratory
5 Findings valuable in decision making
6 Other (Explain

TRAINING AIDS USED, PLANNED OR NEEDED = (TA) in Col. 52
1 Workshops
2 Movies
3 Slides
4 Other
5 None used, but some are needed (Explain)

PART C

55 56	57 62	63 64	65	66 67	68 69	70 73	74 77	78 79	80
Reg. State	Benefit End Date Mo. Day Yr.	Num. Mo.	SB	Accid. Prev.	Lives Saved	Cash $ Saved	User $ Saved	Ben/C	Ys No
0 3									1

State Reporting Implement.

DID RESEARCH PAY OFF - Col. 80
If no estimate is possible, do you feel that benefits substantially exceeded the cost? Enter code, Yes = 1, No = 2

BENEFIT/COST RATIO (For reporting period)
Enter in Col's. 78 & 79, to nearest unit $, the benefits per research dollar invested

TIME PERIOD OF SAVINGS & BENEFITS
Period ending date - Col's. 57 - 62
Total period in months - Col's. 63 & 64

BEST EST. OF $ SAVINGS THRU IMPLEMENTATION
Enter agency savings ($1000) in Col's 70 - 73
Enter user savings ($1000) in Col's 74 - 77

TYPE OF SAVINGS OR BENEFITS = (SB) in Col. 65
1 Cash savings to agency
2 Highway user savings (monetary)
3 Savings probable but difficult to assess
4 Improved safety or convenience
5 Improved aesthetics, environmental aspects
*

* For combination benefits, see manual for codes.

ESTIMATED No. of ACCIDENTS PREVENTED & No. of LIVES SAVED
No. of Accidents in Col's 66 & 67
No. of Lives saved in Col's 68 & 69

8	9 80
Card	R & D Study Title
B	IMPLEMENTED PART OF RECOMMENDATIONS - CONTINUING COMPOSITION
C	STUDIES
D	

NOTE - Type no more than 72 characters (Elite) per line including all spaces and punctuation. Use ALL CAPS

NOTE - Type no more than 72 characters (Elite) per line, including all spaces and punctuation. Use all **CAPS**

8	9 80
Card	Study Objectives
G	OBTAIN STRESS RELAXATION MODULI, CHEMICAL COMPOSITION DATA, & MOLECULAR
H	WEIGHT. CORRELATE THE EMPIRICAL PHYSICAL PROPERTIES WITH CHEMICAL
I	COMPOSITION ANALYSIS. DETERMINE IF RELATIONSHIPS EXIST BETWEEN CHANGES
J	IN PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION AS A FUNCTION OF AGE.

8	9 80
Card	Study Findings
M	REGRESSION ANALYSIS CAN BE USED TO CORRELATE EMPIRICAL PHYSICAL
N	PROPERTIES TO CHEMICAL PROPERTIES. ASPHALTENE CONTENT INCREASES
O	WITH AGE WHILE OTHER FRACTIONS DECREASE. EMPIRICAL PHYSICAL
P	PROPERTIES CAN BE PREDICTED FOR AN ASPHALT OF A GIVEN AGE BASED
Q	ON KNOWLEDGE OF THE CHEMICAL COMPOSITION.
R	

8	9 80
Card	Implementation - How Done
V	THE DEPARTMENT IS CONTINUING THE COMPOSITION STUDIES FOR EACH
W	ASPHALT THROUGHOUT THE LIFE OF THE PAVEMENT. POSSIBLY A
X	SPECIFICATION CAN BE DEVELOPED FOR A BETTER PAVING-GRADE
Y	ASPHALT.
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16. Abstract

Samples of paving-grade asphalts from eleven different paving projects in the State of Arkansas were subjected to physical and chemical investigations to determine the stress relaxation moduli, chemical composition, and the molecular weight of the chemical fractions. The stress relaxation moduli were determined by means of a rotational conicylindrical viscometer, the chemical compositions were determined by means of a chromatographic separation technique, and the molecular weights of the fractions were determined by means of the melting point depression of a pure solvent method. A step-wise regression analysis was performed to correlate physical properties such as viscosity, ductility, and penetration with the chemical properties such as composition and molecular weight. An attempt was made to determine how the foregoing chemical properties varied with sample age.

The regression analysis yielded 206 linear equations of which 114 or 55.3% had a multiple correlation coefficient of 75% or higher. The aging studies indicated that the chemical properties generally changed as the samples aged to the detriment of desirable physical properties.

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FINAL REPORT
Highway Research Project #21

CORRELATION OF PHYSICAL PROPERTIES WITH CHEMICAL COMPOSITION OF PAVING GRADE ASPHALTS

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University of Arkansas

in cooperation with

The Arkansas State Highway Department

and

U.S. Department of Transportation
Federal Highway Administration

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DISCLAIMER STATEMENT

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of The Arkansas State Highway Department or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

ABSTRACT

Samples of paving-grade asphalts from eleven different paving projects in the State of Arkansas were subjected to physical and chemical investigations to determine the stress relaxation moduli, chemical composition, and the molecular weight of the chemical fractions. The stress relaxation moduli were determined by means of a rotational conicylindrical viscometer, the chemical compositions were determined by means of a chromatographic separation technique, and the molecular weights of the fractions were determined by means of the melting point depression of a pure solvent method. A step-wise regression analysis was performed to correlate physical properties such as viscosity, ductility, and penetration with the chemical properties such as composition and molecular weight. An attempt was made to determine how the foregoing chemical properties varied with sample age.

The regression analysis yielded 206 linear equations of which 114 or 55.3% had a multiple correlation coefficient of 0.75 or higher. The aging studies indicated that the chemical properties generally changed as the samples aged to the detriment of desirable physical properties.

HRC #21 was a companion project to HRC #17, "Changes in Physical Properties of Asphalt Cement under Service Conditions". Samples selected for HRC #17 were divided and also used in HRC #21.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided for this project by The Arkansas State Highway Department and the Federal Highway Administration.

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INTRODUCTION

"We are all familiar with the many products derived from petroleum which contribute so much to our modern economy and way of life, but few may realize that bitumen (asphalt) was the first petroleum product used by man. Archeologists have determined that asphalt was used as an adhesive and waterproofing material by the civilizations along the Euphrates River as early as 3800 B.C. Bitumen was also used in Eqypt in approximately 2500 B.C. The asphalts used by these civilizations came from deposits in Asia Minor located in the general region of the oil fields that are now a large factor in the world production of petroleum." (20).

A search through the literature of highway history failed to record the use of asphalt for paving purposes between the ancient days and the nineteenth century. The early turnpikes of the eighteenth and nineteenth centuries were the forefunners of the later Good Roads movement in 1880-1900, and have been described in many publications. The roads of this period were mainly constructed of stone or gravel, or of materials which would compact and support the loads transported.

The use of asphalt-based road oil for the surface dressing of highways, as a dust palliative was on the increase in this century across the country, but in many cases it was not an unqualified success. This was due in part to the poor maintenance of the highways, and in part to a lack of knowledge of the asphaltic material itself, as well as how to obtain the best results by its use (11).

In asphaltic concrete, the asphalt binds the aggregate particles together, transmits stresses, and is subjected to fracture, shear, weathering, microbial attack, etc. For these reasons, it was necessary to be able to predict how a given asphalt would perform under road service conditions so that its service life could be estimated. There was some evidence that relationships existed between certain physical properties such as absolute viscosity, penetration, ductility, etc., long used by asphalt technologists as performance criteria, and the chemical composition of asphalt (20).

A need exists for obtaining and correlating the previously mentioned properties to determine mathematical relationships so that the service life and durability of the pavement may be predicted. This information would lead to the design of asphalt highways which would give a longer service life.

Eleven Arkansas paving-grade asphalts were used in the present research. The objectives of this investigation were:

1. To obtain stress relaxation moduli, chemical composition data, and the molecular weights of the various chemical fractions.
2. To correlate the empirical physical properties such as absolute viscosity, penetration, and ductility with the chemical composition analysis.

3. To determine if relationships between changes in the physical properties and chemical composition as a function of aging exist.

Absolute viscosity, ductility, and penetration data used in the regression analysis were provided by Mr. J.R. Bissett of the Department of Civil Engineering. The elasticity, chemical composition, and molecular weight data were obtained from previous work in the Department of Chemical Engineering by Mr. L.W. Shipley and Mr. P.D. Duggar, under the supervision of the author.

LITERATURE SURVEY

A review of the literature concerning the relationship of physical properties to chemical properties showed that Gotolski, et.al., (10) investigated the changes in asphalt properties with "a view to gaining an understanding of the factors affecting the durability of asphalt pavements." They used the Rostler Precipitation Method (17) for the chemical analyses. This method defined asphalt as consisting of five groups of components which could be isolated and the amounts of each determined gravimetrically. These five groups were defined as asphaltenes, nitrogen bases, first acidaffins, second acidaffins, and saturated hydrocarbons. These values were determined by differential weighing and reported as percentages of the total sample weight.

Gotolski, et.al., (10) recognized that the chemical analyses indicated a change in consistency of the asphalt pavement. The asphaltene content appeared to predict the age-hardening of the asphalt. They showed that the maximum asphaltene content was found in the most deteriorated pavement, and it was noted that trends were established to indicate a maximum limit of asphaltenes that a pavement could tolerate and still be serviceable.

The Corbett-Swarbrick separation technique has proven useful in studies concerning the aging and durability of asphalts. (5) However, as far as can be ascertained, no studies have been reported where the technique has been used to relate composition to empirical physical and rheological properties.

Jones (12) found in composition studies using the method developed by Tucker and Schweyer (22) that the lower molecular weight compounds were converted into asphaltenes and heavy aromatic compounds. The composition was found to change more significantly during field processing than during the first six months of road service.

Lamb (13) performed a regression analysis on rheological properties which he had determined by sliding-plate microviscometer and not the empirical properties used in this study. His results yielded significant relationships, but the composition data alone were not sufficient to describe the flow behavior at temperatures below 120°F. It was concluded that the flow behavior of asphalts at lower temperatures was more dependent on factors such as association and colloidal state than on the relative content of specific types of compounds.

SURVEY OF ANALYTICAL PROCEDURES

1. Chemical Composition:

One of the most important indicators of the performance of a paving asphalt is its chemical composition. Recent studies (10) show a relationship between chemical composition and pavement durability.

In the Rostler Precipitation Method, asphalt is divided into five groups of components which can be isolated and quantitatively determined. This method makes a sharp division between resins and oily fractions, and then further subdivides the resinous fractions. The principal feature of this method is that the fractions determined are well-defined groups of like chemical activity. The use of this division process reveals not only the differences between fractions but also what changes occur during aging and in-service exposure. The changes are given in terms of percent change in composition, particularly in percent change of asphaltene content as it relates to durability; i.e., embrittlement or hardening.

A later work of Rostler and White (17) presents an analysis of asphalt as consisting of five basic constituents; namely, asphaltenes, nitrogen bases, first acidaffins, second acidaffins, and saturated hydrocarbons. By precipitation, this method isolates these five constituents, the values of which are determined by differential weighing and then reported as percentages of the total sample weight. The samples of original and recovered asphalt cements were analyzed by Gotolski using this method (10).

Chemical analyses appear to be good indicators of change in consistency of the asphalt components in the pavement. The asphaltene content, which is usually the first fraction in the test, appears to be an adequate indicator of the age-hardening of the asphalt. Increases in asphaltene content are generally manifested by decreases in penetrations, decreases in ductility, and increases in absolute viscosity.

In addition to asphaltene content, the combination of components may be a determining factor. Gotolski (10) states that some investigators have shown that a preponderance of nitrogen based (N) compounds will result in an asphalt exhibiting very rapid embrittlement. A high concentration of first acidaffins (A_1) will result in an asphalt that will undergo the greatest change in composition with time. An asphalt containing a high concentration of second acidaffins (A_2) appears to be least affected. Saturated hydrocarbons (H_s) in small to moderately large amounts are beneficial. However, saturated hydrocarbons in excessive amounts result in a product which lacks cohesion and ceases to be an asphalt. (10)

The ratio $(N + A_1)/(A_2 + H_s)$ should be considered only a first approximation for an expression relating composition to durability. (17)

The Corbett-Swarbrick separation technique has proven useful in studies concerning the aging and durability of asphalts. (5) However, as far as can be ascertained, no studies have been reported where the technique has been used to relate composition to empirical rheological properties. Unfortunately, there is no way to determine a priori whether a particular composition technique will prove useful in such studies.

Previous work has shown that viscosity should be a function of the ratio of resins to saturates. In terms of the fractions obtained from the modified Corbett-Swarbrick technique, the ratio would be HA/PN. The dispersion coefficient as defined by Traxler (21) was approximately equivalent to the ratio (LA + HA)/(HX + PN). This coefficient was used to correlate composition with durability of asphalt.

Exact comparison of the fractions obtained by various separation methods is not possible because of the different techniques used. For example, the HA fraction obtained by the Corbett-Swarbrick method and the resins fraction obtained by the Traxler-Schweyer method (21) are both considered to be highly aromatic materials which tend to peptize the asphaltenes. However, it is highly probable that if the two fractions were obtained from the same asphalt they would not be identical in either quantity or chemical nature. (13).

2. Solvent Extraction and Chromatography:

Solvent extraction methods employ the principle that part of the maltenes are soluble in a solvent at a particular temperature and insoluble in a different solvent or in the same solvent at a different temperature.

The method used in this investigation was a modification of one first used by Tucker and Schweyer (22). They had changed the original Corbett and Swarbrick method. (5) The original asphalt sample was extracted with n-hexane to separate the maltenes from the asphaltenes. Asphaltenes were the hard materials which were insoluble in n-hexane, and since they were separated by n-hexane they were called hexa-asphaltenes. These compounds are believed to be multi-ring aromatics with very short aliphatic side chains and were characterized by a high molecular weight (approximately 3000). They were considered to be oxidation products since the HX fraction has been found to increase with air-blowing and with weathering in road service.

Maltenes are composed of soft resins, oils, hard resins, and waxes. They contain paraffin and naphthene hydrocarbons with alkyl side chains, aromatic compounds with aliphatic side chains, and simple multi-ring compounds (12).

Most chromatographic separations are basically the same. The asphaltenes are precipitated with a light weight hydrocarbon such as pentane or hexane. The maltenes are then added to a chromatographic column packed with an adsorbent solid. The heavier components are selectively drawn to the surface of the adsorbent. By successive elutions with selective solvents at controlled temperatures, the maltenes are separated into fractions of different molecular weights.

Corbett and Swarbrick (6) developed a short-cut method which separated asphalt into three components. The analysis could be performed in an eight-hour day. The asphaltenes were separated from the maltenes by refluxing with n-hexane. The maltenes were fractionated further into paraffins plus naphthenes and aromatic oils in a chromatographic column packed with an activated alumina called Porocel. The maltenes were added to the column, which was controlled at 150±5°F and then the saturated hydrocarbons were eluted with iso-octane. Pyridine was used to wash the aromatic oils from the column. One of the main advantages of this method was that it yielded very clean-cut fractions.

In a later investigation, Corbett and Swarbrick (7) modified their technique to get five fractions. The asphaltenes and maltenes were separated as previously mentioned. The paraffin plus naphthene (PN) fraction was eluted with n-heptane. Then the single-ring aromatic compounds (SRA) were removed with a mixture of heptane and benzene. Benzene was used next to extract the low molecular weight multi-ring compounds (LMA). Heavy multi-ring compounds (HMA) were washed from the column with pyridine. Corbett and Swarbrick used various analytical tools such as infrared and ultra-violet spectrometry, electron and nuclear magnetic resonance, molecular weight, and mass spectroscopy to help identify general characteristics of the compounds common to each fraction.

A brief summary of the characteristics of the fractions follows: (7)

PN fraction - a mixture of paraffins plus naphthene hydrocarbons with alkyl side chains with an average MW of <u>600</u>.

SRA fraction - single ring aromatic compounds with several long aliphatic side chains having an average MW of <u>674</u>.

LMA fraction - a mixture of multi-ring aromatics with much shorter aliphatic side chains than above having an average MW of <u>708</u>.

HMA fraction - a mixture of multi-ring compounds similar to LMA, but having an average MW of 956.

HX fraction - multi-ring aromatics with very short aliphatic side chains having an average MW of 3000.

Tucker and Schweyer (22) used a modified version of Corbett and Swarbrick's method. The asphaltenes were precipitated with n-hexane. The maltenes were subjected to liquid chromatography using heptane as the first solvent at a column temperature of 45±1°C. A paraffin-naphthene (PN) fraction was obtained. The first aromatic fraction was eluted with benzene and was called the light aromatic fraction (LA). The column temperature next was increased to 65±1°C. before the remaining aromatic fractions were removed. The first heavy aromatic fraction (HA_1) was eluted with 1-butanol. Benzene was used to wash the final heavy aromatic fraction (HA_2) from the column (12).

Majors and Couper (14) eluted the column residue with methyl iso-butyl ketone to complete the maltene recovery.

3. Molecular Weight.

Majors and Couper (14) stated that a need has arisen to characterize the asphalt fractions or identify the groups of chemical compounds separated. Certain characterization techniques have been used such as X-ray diffraction, electron spin resonance spectrometry, nuclear magnetic resonance spectrometry, mass spectrometry, elemental chemical analysis, and molecular weight determinations (14). It was decided that the latter two techniques produced useful results at a relatively low cost.

Molecular weight determination is a more direct characterization technique, since the asphalt fractions obtained by various methods are mixtures of compounds, many of which contain long-chain polymeric species. These polymeric materials cause molecular weights determined by various methods to have different values (see page 16). It is absolutely necessary that the technique selected for molecular weight determination must be applicable to all fractions of the asphalt with a reasonable degree of accuracy.

Glasstone (9) detailed Rast's Micro-Method for determining organic molecular weights, selecting camphor as the pure solvent. Camphor was used since the molar depression constant was unusually high, viz. 40. The use of this substance as a solvent for cryoscopic work was proposed by A. Jouniaux (1912); subsequently K. Rast (1922) described a method for the determination of molecular weights using small amounts only of substances soluble in molten camphor. A few milligrams of the experimental material were mixed with about ten times their weight of camphor and the whole mass melted; after re-solidification, the mixture was finely ground and a quantity transferred to a capillary tube such as was commonly used for the determination of melting points. The tube was then attached to an ordinary thermometer and the temperature raised in the usual manner, e.g., in a small sulfuric acid or paraffin bath. The point at which the last traces of camphor were completely melted was recorded as the melting temperature of the solution, for this was the point at which the liquid solution was in equilibrium with a small amount of solid solvent.

The depression of the melting point from that of pure camphor, measured in the same manner, was of the order of 10^{o} or more, and so could be read with sufficient accuracy on a thermometer graduated in units of one degree.

This was the method picked to be the most convenient and to have the least number of limitations for this project. It was adopted with slight modifications, (p. 16) and used for all molecular weight determinations.

4. Elasticity:

Lamb (13) and Miller (15) used a rotational conicylindrical viscometer to measure stress relaxation at a constant strain for paving-grade asphalts. The equipment was designed and built by Buechley (3).

Lamb (13) stated that the essential feature of the conicylindrical viscometer was that the conical ends were designed such that the mean stress and shear rate in the conical sections were equal to those in the cylindrical section. The effective mean radius of the cylindrical section is defined:

$$r_m = \left(\frac{2a^2b^2}{a^2+b^2}\right)^{\frac{1}{2}} \qquad (1)$$

r_m = mean radius of annulus (cm)

a = radius of stator (cm)

b = radius of rotor (cm)

When the radii of the rotor and stator are specified and the half-angle of the rotor cone is fixed at 90°, the angular separation of the stator and rotor may be determined by trial-and-error from the relationship:

$$\delta = f \cos \delta/2 + f^3 \cos \delta/2 \; (3/8 \cos^2 \delta/2 - \tfrac{1}{2}) \qquad (2)$$

δ = angular separation (radians)

$f = (b^2-a^2)/(b^2 + a^2)$

The half-angle of the stator cone is:

$$\Theta = \pi/2 - \delta \qquad (3)$$

Θ = angle of stator cone (radians)

π = pi (3.14159)

The strain imparted to the sample by rotation of the rotor is:

$$\varepsilon_o = \gamma/f \tag{4}$$

ε_o = sample strain (radians)

γ = angular displacement of rotor (radians)

The mean stress is:

$$F' = \frac{T'}{2\pi r_m^2 h_o (1 + 2r_m)/(3h_o \cos \delta/2)} \tag{5}$$

T' = torque (dyne-cm)

$h_o = h_1 + 2 \left[a \cot \theta - r_m \cot (\theta + \delta/2) \right]$

h_1 = length of inner cylinder (cm)

The stress relaxation modulus is obtained by dividing Equation (5) by Equation (4)

$$G_r = \frac{F'}{\varepsilon_o} = \frac{T'}{2\pi r_m^2 h_o (1 + 2r_m)/(3h_o \cos \delta/2)} \quad \frac{f}{\gamma} \tag{6}$$

G_r = stress relaxation modulus (dynes/cm^2)

G_r is a function of time when T is used as a function of time.

DISCUSSION OF ANALYTICAL THEORY

1. Molecular Weight

Three methods of molecular weight determination were investigated before a suitable method was selected.

The first method was the ebullioscopic or boiling point elevation method (9). The principle behind this procedure was that a definite weight, w_2, of solute, whose molecular weight was to be found, was dissolved in a known weight, w_1, of solvent and the elevation of boiling point, ΔT_e, was measured; since the molecular elevation constant, K_e, could be obtained from proper standard tables, M_2, the molecular weight of the solute could be calculated by:

$$M_2 = K_e \frac{1000\ w_2}{\Delta T_e\ w_1} \tag{7}$$

It was found that this method was very sensitive to the amount of solute. The technique required a relatively large sample of solute to produce an appreciable boiling point elevation. The small amounts of the asphalt fractions available were not large enough to use in the determination.

The second method considered involved an ultracentrifuge technique, based upon the sedimentation equilibrium principle (23). The method made use of the following equation:

$$\bar{M}_w = \frac{2RT}{(1-\bar{v}\rho)\omega^2} \left(\frac{d\ln c}{d(x^2)}\right) \tag{8}$$

where $\bar{M}_w$ = weight average molecular weight of solute for polydisperse solute.

R = gas constant (8.313×10^7 ergs/degree mole)

T = absolute temperature, $^{\circ}K$

$\bar{V}$ = partial specific volume, cc/g-mole

ρ = density of solution,grams/cc

ω = angular velocity,radians/sec

c = concentration, g/cc

x = distance from axis of rotation, cm

Equation 8 is the kinetic description of sedimentation equilibrium and treats equilibrium as a state in which transport in a centrifugal direction is completely counterbalanced by transport in a centripetal direction (2).

This technique was investigated using the Beckmann Model E Ultracentrifuge located in the Virology Laboratory of the College of Agriculture and Home Economics at the University of Arkansas. It was found to be most applicable to high molecular weight materials in the range of 20,000 and above. Since the heaviest asphalt fraction, HX, was only in the 2,000-3,000 range, the technique was not applicable.

The third method, and the method subsequently used, was the melting or freezing point depression method.

Since a non-volatile solute lowers the vapor pressure of a solution, it followed that the freezing point of the solution was lower than that of the pure solvent. The fact that a dissolved substance depressed the freezing point of water had been known for many years, and in 1771 R. Watson observed that the time taken for a salt solution to freeze, and hence presumably the lowering of the freezing point, was proportional to its concentration. The same general conclusion was reached by C. Blagden (1788) and hence the proportionality between the lowering of the freezing point and the concentration of the solution has been called Blagden's Law (9).

The equation used to determine weight-average molecular weight is as follows:

$$M_2 = K_f \frac{1000\ w_2}{\Delta T_f\ w_1} \tag{9}$$

This is identical to the boiling point elevation equation (8) with the exception of K_f instead of K_e. K_f can also be found in standard tables and freezing points can be determined with great accuracy. Also, this method is not as sensitive to the amount of solute as is the ebullioscopic method.

It has been noted by Majors and Couper (14) that the value of the molecular weight of a fraction determined by a given molecular weight technique cannot be compared absolutely with the numerical value obtained by another molecular weight technique (see page 11).

The molecular weights found by the various methods may be either weight-average or number-average.

The weight-average molecular weight is defined:

$$\bar{M}_w = \frac{\sum_{i=1}^{n} n_i M_i^2}{\sum_{i=1}^{n} n_i M_i} \tag{10}$$

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

n_i = number of molecules of molecular weight M_i.

The number-average molecular weight is defined:

$$\bar{M}_N = \frac{\sum_{i=1}^{n} n_i M_i}{\sum_{i=1}^{n} n_i} \qquad (11)$$

$\bar{M}_N$ = number-average molecular weight

Other terms are the same as for Equation 10.

$\bar{M}_w$ and $\bar{M}_N$ may differ by several orders of magnitude depending upon the relative numbers and sizes of the individual chemical species involved in the polydisperse (non-uniform particle size) system (23).

2. Elasticity:

Lamb (13) states that numerous techniques and mathematical relationships have been developed to measure or characterize the rheological behavior of materials which exhibit both elasticity and flow. These materials are said to be viscoelastic since they can be regarded neither as ideal elastic solids nor as viscous liquids, but instead partake somewhat the character of both.

In the section of his dissertation entitled "General Viscoelastic Theory," Lamb (13) states that two types of viscoelastic testing are encountered, static and dynamic. The former consists of a test involving the transient response to stress or strain; the latter is a sinusoidal or vibrational type of test. Specific test applications determine which is preferable. Materials which have a high resistance to flow are especially amenable to the static test known as stress relaxation (24).

In this technique, the sample is instantaneously deformed to a certain strain, and the decrease, or relaxation of the stress with time is observed. The curve of stress as a function of time constitutes the stress relaxation.

The ratio of time dependent stress to strain is denoted by $G_r(t)$ for shear. This ratio for elastic solids is known as Young's Modulus. A convenient method of presenting stress relaxation data is to plot the logarithm of the relaxation modulus (G_r) as a function of the logarithm of time until relaxation approaches an asymptote (13).

THEORETICAL DISCUSSION

A regression analysis technique was used to relate the various physical properties to the chemical composition of the asphalt samples.

Curve fitting is another name for regression. It is a technique for deriving a formula or equation based on a large amount of data for several variables. It gives a simple equation for one of the quantities in terms of the others. The final equation brings out relationships, summarizes the data, and may be used to predict new or future situations.

The variability in data is generally accounted for by errors in measuring instruments, inherent randomness of human action, oversimple formulas that leave out many smaller interacting variables, and gross mistakes. Regression accounts for the variation in the development of the regression equation.

The regression analysis used to relate the physical properties of the asphalts to the chemical properties involves the method of "least squares," which resembles polynomial interpolation. The least square or regression curve approximates a given set of data points so that the sum of the squares of the distances from the individual data points along the ordinate to the curve is a minimum (18).

For example:

To find the least squares approximation for the function, $F(x) = \alpha + \beta x$, it is required to determine the values of α and β which minimize the sum of the squared ordinate-deviations between observed and estimated values. To do this, the sum of the squared differences between observed and theoretical values is,

$$s(\alpha,\beta) = \sum_{i=1}^{n} (y_i - \alpha - \beta x_i)^2 \qquad (12)$$

s(α,β) is a function of α and β; consequently, if it is to be minimized, it is required that,

$$\frac{\partial s}{\partial \alpha} = \frac{\partial s}{\partial \beta} = 0 \qquad (13)$$

The required estimates for the constants will be found by equating,

$$\frac{\partial s}{\partial \alpha} = -2 \sum_{i=1}^{n} (y_i - \alpha - \beta x_i) \qquad (14)$$

and

$$\frac{\partial s}{\partial \beta} = -2 \sum_{i=1}^{n} x_i (y_i - \alpha - \beta x_i) \qquad (15)$$

to zero.

Simplification of Equation 15 gives,

$$\sum_{i=1}^{n} y_i = na + b \sum_{i=1}^{n} x_i \qquad (16)$$

$$\sum_{i=1}^{n} x_i y_i = a \sum_{i=1}^{n} x_i + b \sum_{i=1}^{n} x_i^2 \qquad (17)$$

These equations give a line $f(x) = a + bx$ which is the least squares estimate for the original $F(x) = \alpha + \beta x$. (19)

This same technique can be used with quadratic and higher-degree equations, but involves more complexity in the regression analysis. Due to this complexity, a linear fit was attempted in this determination.

The regression analysis used in this study was in the form of a computer program available from IBM. A step-wise regression analysis of 9999 sets of observations of one dependent variable and of 57 explanatory (independent) variables gave an output of means, standard deviations, simple correlation coefficients, and step-wise results.

Step-wise results consisted of the standard error of estimate, the multiple correlation coefficient, F, constant term, and regression coefficients.

The program offered the following advantages:

1. The step-wise method of computation was employed, which was more powerful than standard computational methods as a means of unmasking underlying relationships between variables.
2. Original data could be transformed in nine different ways. Algebraic transformations of original data have sometimes been found useful in cases where non-linear relationships exist.
3. Simple correlation coefficients were printed for every pair of variables.
4. Residuals (difference between actual value of dependent variable and its regression equation estimate) could be printed for each observation.

The following are explanations of the quantities provided by the regression analysis.

A. Standard Deviation, s:

The degree to which numerical data tend to spread about an average value is called the variation or disperson of the data.

The standard deviation of a set of N numbers x_1, x_2, . . . x_N is denoted by s and is defined by

$$s = \sqrt{\frac{\sum_{j=1}^{n} (x_j - \bar{x})^2}{N}}$$

$\bar{x}$ = mean of x_j,s

Thus s is the root mean square of the deviations from the mean or, as it is sometimes called, the root mean square deviation (19).

The square of the standard deviation is called the variance and is denoted by s^2.

B. Simple Correlation Coefficients:

The quantity ρ_{xy} is a measure of the association between the random variables x and y. It can be shown that $-1 < \rho_{xy} < 1$. For example, if $\rho_{xy} = 1$, x and y are "perfectly" positively correlated and the possible values of x and y all lie on a straight line with positive slope in the (x,y) plane. If $\rho_{xy} = 0$, the variables are said to be uncorrelated, that is, unassociated with each other. This does not mean that x and y are statistically independent, as most elementary textbooks emphasize. If $\rho_{xy} = -1$, x and y are perfectly negatively correlated and the possible values of x and y again all lie on a straight line, with negative slope, in the (x,y) plane (8).

$$\rho_{xy} = \frac{\text{covariance }(x,y)}{\{V(x)V(y)\}^{\frac{1}{2}}} \qquad (19)$$

where if f(x,y) is the continuous joint probability distribution of x and y,

$$\text{covar }(x,y) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \{y-E(y)\}\{x-E(x)\}\ f(x,y)\ dxdy \qquad (20)$$

and

$$V(y) = \int_{\infty}^{\infty}\int_{\infty}^{\infty} \{y-E(y)\}^2\ f(x,y)\ dydx \qquad (21)$$

where

$$E(y) = \int_{\infty}^{\infty}\int_{\infty}^{\infty} yf(x,y)\ dydx \qquad (22)$$

C. Standard Error of Estimate, S:

The residual mean square, S^2, is an estimate of $\sigma_{x.y}{}^2$, the variance about the regression. Before and after adding a variable to the model, we can check

$$S = \sqrt{\text{residual mean square}} \qquad (23)$$

Examination of this statistic indicates that the smaller it is, the better, i.e., the more precise will be the predictions. Since S can be made zero by including enough parameters in the model -- just as R^2 can be made unity -- this criterion must also be used cautiously. Reduction of S is desirable where possible (8).

D. Multiple Correlation Coefficient, R :

$$R^2 = \frac{\left\{ \sum_{i=1}^{n} \left[(x_i - \bar{x})(y_i - \bar{y}) \right] \right\}^2}{\left[\sum_{i=1}^{n} (x_i - \bar{x})^2 \right] \left[\sum_{i=1}^{n} (y_i - \bar{y})^2 \right]} \qquad (24)$$

x_i, y_i = quantities related by regression

$\bar{x}, \bar{y}$ = average of x_i, y_i

R^2 is a measure of the goodness-of-fit in regression work. If $R^2 = 0.78$, then 78% of the variation of y about its <u>average</u> is explained or determined by the regression in terms of x_i, x_2, x_3 . . . . R^2 is also called the coefficient of determination. The square root, R, is known as the multiple correlation coefficient (4).

E. Goodness-of-Fit, F:

To find the distribution of the ratio of the variances of two independent random samples, the F-test is used. This test determines whether two samples come from populations having equal variances. If they do, the two sample variances should be nearly the same; that is, their ratio should be close to 1.0. To determine the F distribution, the following formula is used:

$$F = \frac{s_1^2}{s_2^2} \qquad (25)$$

s_1, s_2 = variances of independent random samples of size

n_1 and n_2, respectively, taken from two normal populations having the same variance.

The F distribution has two parameters, ν_1, the degrees of freedom for the sample variance in the numerator, and ν_2, the degrees of freedom for the sample variance in the denominator (17).

$$\nu_1 = n_1 - 1 \tag{26}$$

$$\nu_2 = n_2 - 1$$

As reported in the regression analysis, the Goodness-of-Fit term is given as the F value of the ratio of mean square attributable to independent variables over residual mean square.

The output from the program gives an equation of the form:

$$y = a + b_1 x_1 + b_2 x_2 + \ldots + b_n x_n \tag{28}$$

where y is the dependent variable such as absolute viscosity, penetration, ductility, etc., a is the regression constant term, b_n the regression coefficients, and x_n the independent variables which are compositions or molecular weights. (See Appendix III.)

Therefore, the chemical properties of asphalt would have an effect on the empirical physical and rheological properties of asphalt. The technique of regression analysis was found to be a convenient method of correlating the chemical variables with the physical properties.

The two primary chemical characterizations employed were the composition of the samples and the molecular weight of the component chemical fractions. An attempt was made to use regression analysis to determine what effect the relative amounts of the chemical composition fractions had on the properties such as absolute viscosity, ductility, and penetration. Likewise, the regression analysis was used to determine the effect of the molecular weight of the composition fractions on the physical properties mentioned above.

DESCRIPTION OF EQUIPMENT

The equipment used in this study for the fractionation of asphalt samples was identical to that used by Majors (14). The method involved three major steps: solid-liquid extraction, chromatographic separation, and evaporation.

Extraction of the asphalt samples was carried out using a 250-ml Erlenmeyer flask with a 24/40 ground glass fitting, a 40-mm x 300-mm Sohxlet extractor with ground glass fittings, and a 700-mm Liebig condenser, (Fig. 1). Heating of the flask was accomplished by means of a 140-watt Glas-Col heating mantle with power being supplied by a Staco 10-ampere variable autotransformer, type 2PF 1010. Cooling water for the condenser was obtained from the city water supply.

The chromatographic separation of the maltenes was accomplished in three water-jacketed glass columns. The columns were 48 inches long fitted with a jacket length of 48 inches. The inner, packed tubes were of 15-mm OD glass tubing with a $ 24/40 female joint at the top, and drawn to a 5-mm ID tip at the bottom. Rubber stoppers were used at top and bottom to separate the tubes and maintain concentricity.

Temperature control of the columns was maintained at 45 ± 1.0°C and at 65 ± 1.0°C by circulating water from a 1000-watt Precision Scientific constant temperature bath, #L-5, capable of maintaining temperature of 100 ± 1°C, by means of a 1/3-horsepower centrifugal pump.

Solvent was admitted to the column from a 250-ml separatory funnel fitted into the top at the column by a ₷ 24/40 male ground glass fitting. Fractions were collected in 400 ml beakers or 250 ml Erlenmeyer flasks, depending upon the preference of the operator. (Fig. 2)

The fractions were evaporated to dryness in 100-ml porcelain evaporating dishes on a steam table located inside a fume hood. In some cases, it was necessary to employ an oven to completely dry the fractions.

Two ovens were used. One, a Model B electrically-heated oven from W.H. Curtin and Company at 270 ± 10°F was used to melt samples, dry some fractions, and to activate the Porocel adsorbent. The other, a Blue M Electric Company Model M 15A electrically-heated oven with integral thermocouple capable of maintaining a temperature from 66-1090°F was used for activating the Porocel at 700°F.

Weights of samples and fractions were determined by using a Sartorius Balance, with a range of 0.0000 to 199.9999 grams.

Other miscellaneous pieces of equipment which were employed were: two 75-mm glass funnels fitted with male ₷ 24/40 ground glass joints for packing the columns, funnels, several 100-mm watch glasses for beaker and evaporating dish lids, and 2-dram bottles with screw closure lids for storing the fractions.

The extraction and chromatographic equipment along with the water manifolds and transformers were mounted on an aluminum rod framework attached to the laboratory wall for convenience and ease of operation.

The equipment employed for molecular weight determination consisted of a 3-liter glass vessel containing approximately 2.5 liters of mineral oil, stirred by an air-operated Precision Scientific Aero-Mix agitator to maintain uniform temperature, and heated by a 335-watt Glass-Col heating mantle controlled by the same transformer as listed above. The vessel contained a sheet metal rack fabricated to hold six glass capillary sample tubes. A piece of flat glass was mounted in the vessel wall in front of the sample tubes to minimize optical distortion when visually determining the sample melting points (Figure 6).

Other miscellaneous equipment used was a 400°F thermometer for measuring the temperature of the mineral oil, a ring stand and clamps to support the apparatus, and melting bottles to dissolve the fractions in the camphor. The apparatus was mounted in the fume hood for convenience of operation and safety.

Elasticity measurement equipment was identical to that used by Lamb (13) and Miller (15) and consisted of four major parts: A coni-cylindrical viscometer (Figure 7), a constant temperature bath (Figure 8), a torque sensing device, and a recorder. The viscometer was attached to the bath at the bottom and to a torque-sensing strain gauge at the top.

The temperature control system, shown in Figure 8, was visually monotored continuously by means of a Hewlett-Packard Model #2800A digital readout quartz thermometer.

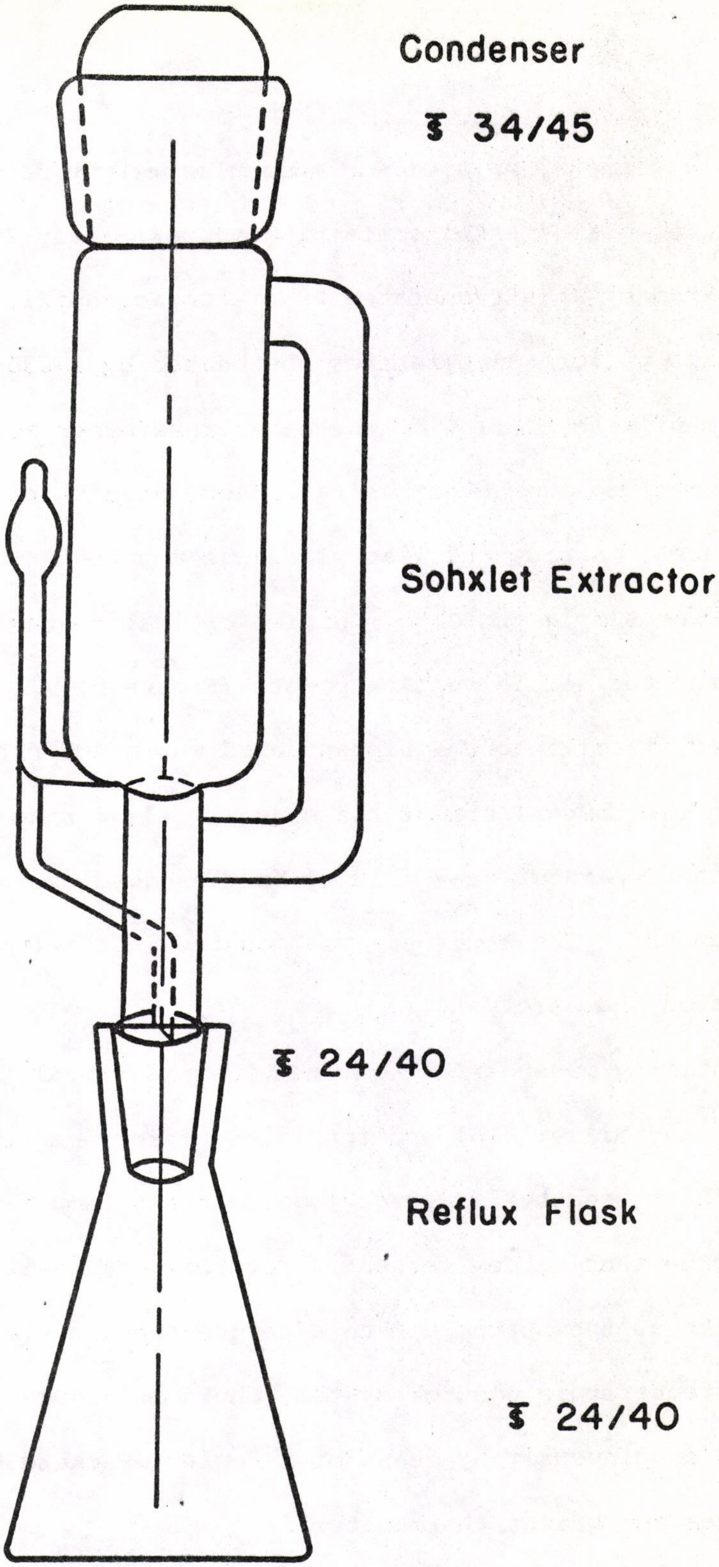

FIGURE 1 Sketch Of Extraction Apparatus

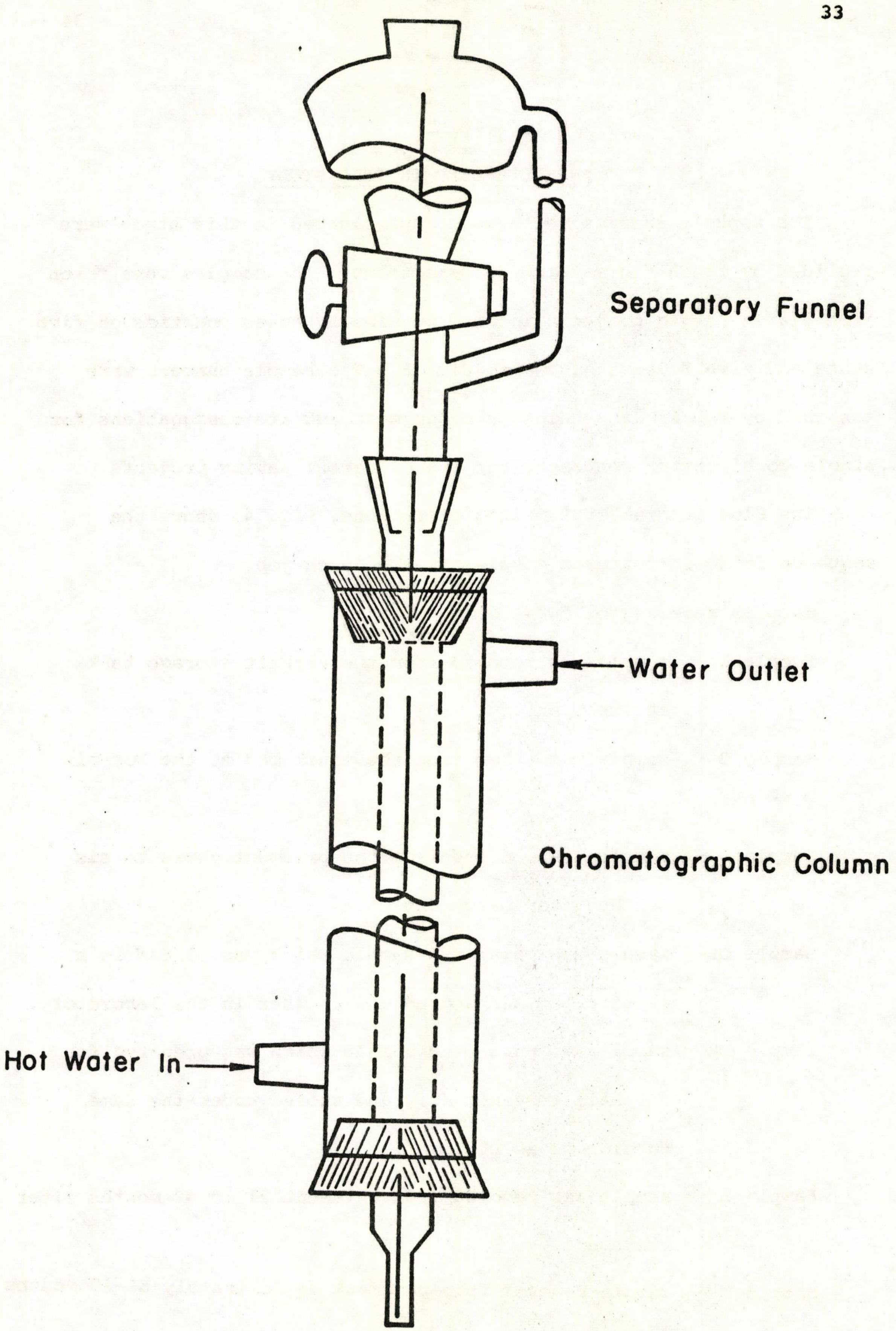

FIGURE 2 Sketch Of Chromatographic Apparatus

ASPHALTS USED IN THIS STUDY

The asphalt samples which were investigated in this study were provided by the Arkansas Highway Department. The samples were taken from eleven paving projects located in nine Arkansas counties on five state and five federal highways, Fig. 3. The sample numbers were assigned by the Arkansas Highway Department and are designations for single construction contracts for the different paving projects.

The Flow Diagram of Sampling Operations, Fig. 4, shows the sequence followed for each sample taken on each job.

Samples were as follows:

Sample A - sample was removed from the asphalt storage tank at the plant.

Sample B - sample was taken from the truck bed at the hot-mix plant.

Sample C - sample was removed from the pavement three to six months after placement.

Sample DL- sample was part of B sample which was placed in a plastic bag and stored under water in the laboratory.

Sample DM- sample was part of B sample which was prepared for Marshall testing, (1), and stored under the same conditions as DL

Sample E - sample was removed from pavement 21 to 42 months after placement.

Sample F - sample removed from pavement approximately 55-60 months after placement.

Sample G - sample removed from pavement approximately 72-78 months after placement.

Details of these samples and similar procedures are to be found in a report prepared by J.R. Bissett (2).

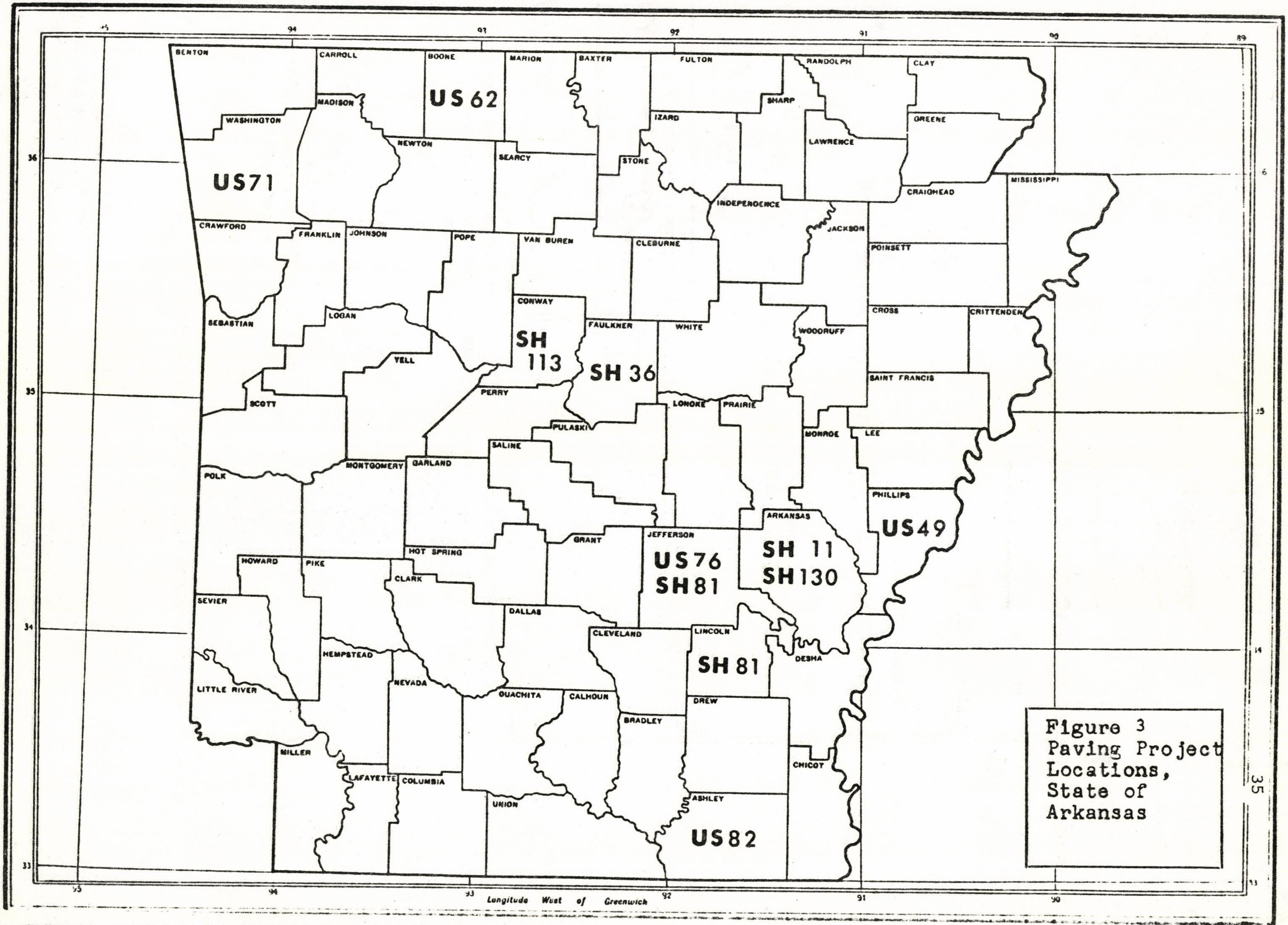

Figure 3 Paving Project Locations, State of Arkansas

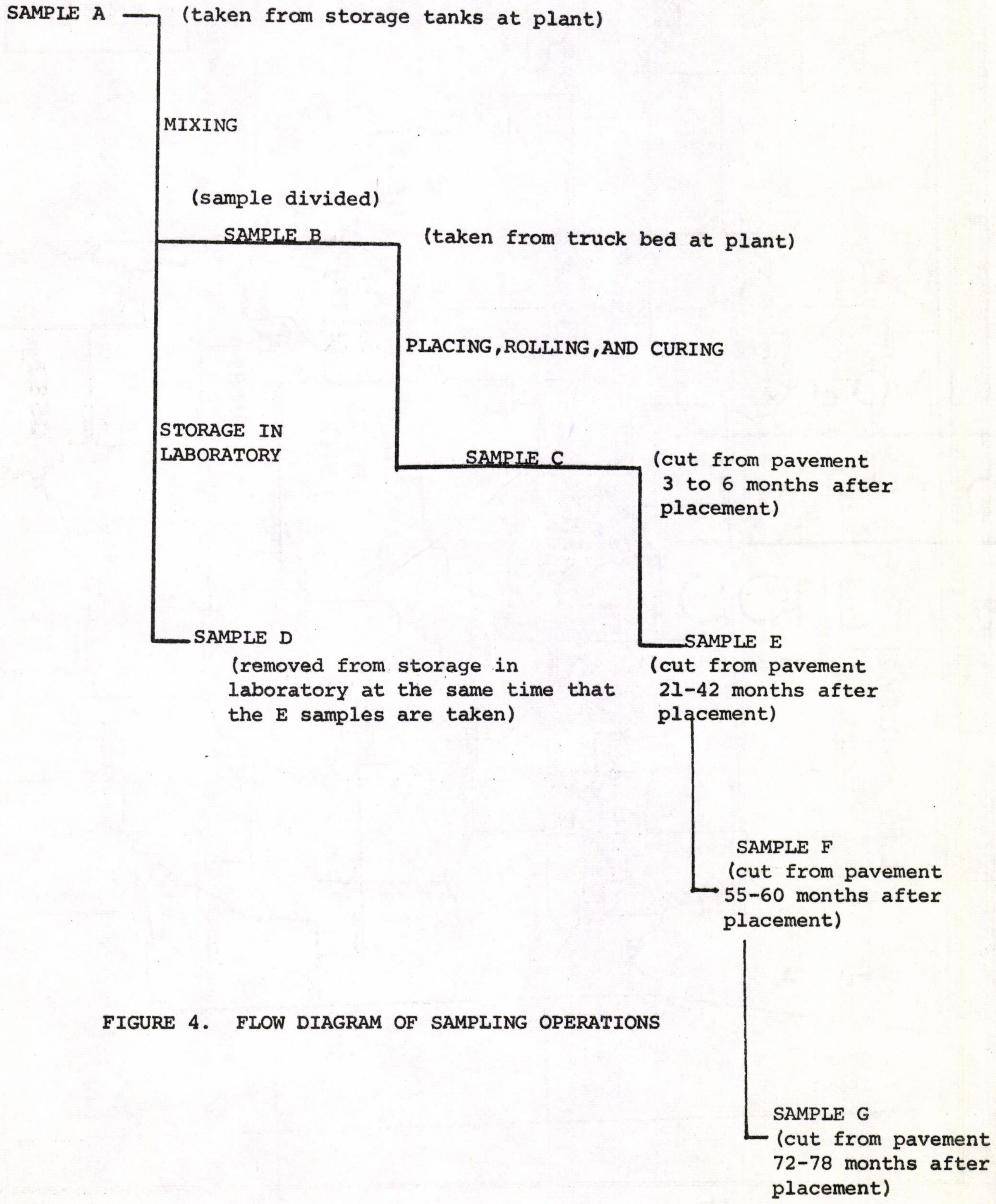

FIGURE 4. FLOW DIAGRAM OF SAMPLING OPERATIONS

OPERATING PROCEDURE

Solvent Extraction and Chromatography:

Extraction of the asphalt to separate the soluble maltenes from the insoluble asphaltenes was carried out in essentially the same manner as that used by Corbett and Swarbrick (6) which was modified by Tucker and Schweyer (23) and subsequently used by Jones (12).

The procedure is as follows:

1. Weigh 1.00 ± 0.05g of the asphalt to be analyzed into the reflux flask, add 75 ml of n-hexane per gram of asphalt, and reflux for one hour. (Figure 1.)
2. Filter the contents of the reflux flask through a Whatman No. 42 filter paper. Collect filtrate in a 400-ml beaker. Wash precipitate with 100 ± 25 ml of n-hexane.
3. Return the precipitate to reflux flask, add 50 ml of n-hexane, and reflux for 30 minutes. Again filter hexane solution, and combine the two filtrates.
4. Extract the hexane insolubles from the filter paper with benzene until the filter paper is clean. Evaporate the benzene, weigh the residue and report the weight as asphaltenes. (HX)
5. Prepare the chromatographic column by packing the inner tube to a height of 36 inches with 20-60 mesh Porocel which has been previously dried in an oven at 700 ± 5 ^{o}F for three hours. (Figure 2). Packing is accomplished by tapping the column with a rubber hammer until no further settlement occurs. Care must be taken to avoid exposure of adsorbent to moisture.

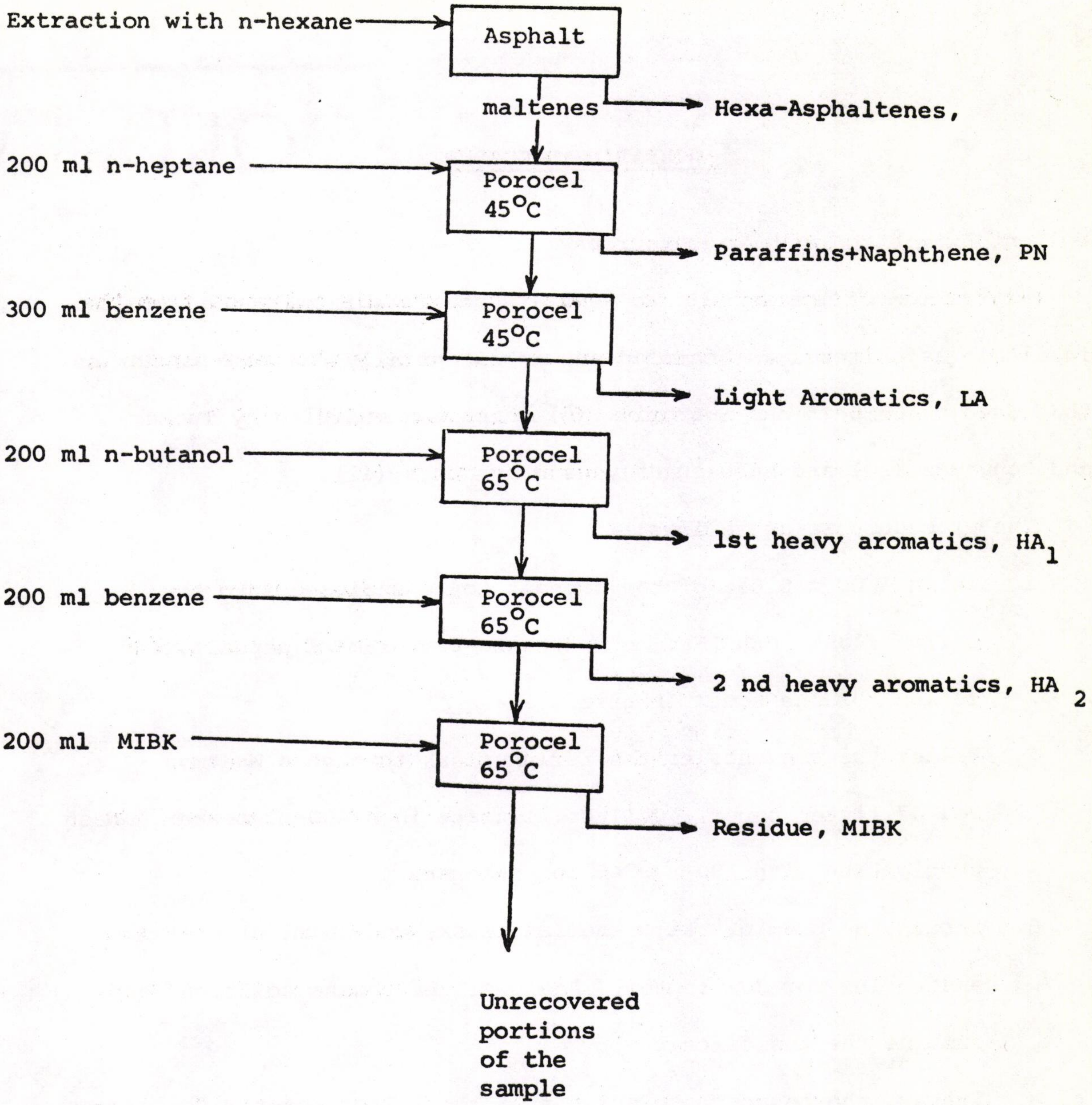

FIGURE 5.STANDARD ASPHALT FRACTIONATION SCHEME

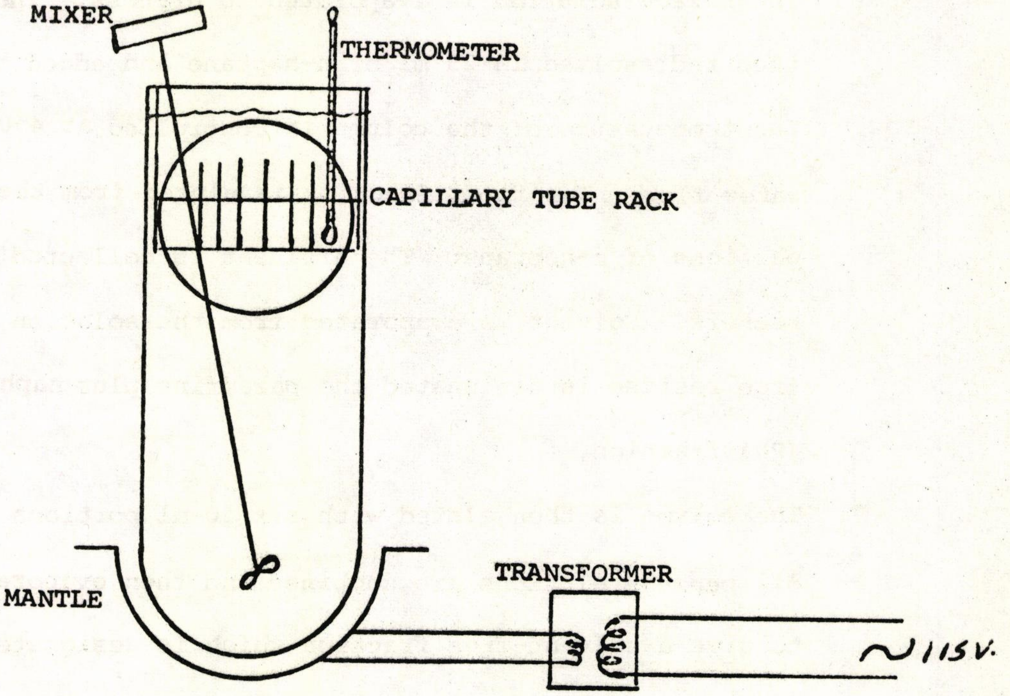

FIGURE 6. MOLECULAR WEIGHT APPARATUS

6. The hexane solution is evaporated to dryness. The residue is then redissolved in 25 ml of n-heptane and added to the column. The temperature of the column is controlled at 450 ± 1 °C by annular water flow. The first fraction is eluted from the column with four 50-ml portions of n-heptane. The effluent is collected in 400-ml beakers. Solvent is evaporated from the solution, and the solvent-free residue is designated the paraffins plus naphthene (PN) fraction.
7. The column is then eluted with six 50-ml portions of benzene. All benzene elutions are combined and then evaporated and dried to give a solvent-free fraction which is designated the light aromatic (LA) fraction.
8. Next the column is heated to 65±1°C with the circulating water, and eluted with four 50-ml portions of n-butanol. The solvent is then evaporated, and the residual material is designated the first heavy aromatic (HA_1) fraction.
9. The second heavy aromatic (HA_2) fraction is eluted from the column by four 50-ml portions of benzene.
10. Finally, the remaining residue is washed from the column with four 50-ml portions of methyl-isobutyl ketone and is designated the MIBK fraction.

Molecular Weight:

The procedure for determining the molecular weights of the asphalt fractions was essentially Rast's Micro Method. (9)

The procedure is as follows:

1. Weigh sample bottle and lid separately and record. Add 1-3 grams asphalt fraction and record weight. Add 2-3 times this weight of USP Grade camphor.
2. Place lid on bottle and heat bottle in heating mantle to liquify contents. During heating some camphor vaporizes and crystallizes on lid, but asphalt fraction does not vaporize appreciably.
3. Cool bottle in air stream. This permits rapid cooling but prevents bottle from cracking.
4. Remove lid, weigh, determine weight of recrystallized camphor, subtract from camphor weight in solution. Determine new camphor-asphalt ratio from new weight of camphor in solution,
5. Remove solid solution from weighing bottle, grind in a porcelain mortar sufficiently fine to place in capillary tubes. Tap crystals loosely into tube, and heat seal ends of tube.
6. Heat oil bath to approximately 200°F. Melting points should be in the range of 250-350°F.
7. Follow solution preparation procedure, steps 1-6, for each of the six asphalt fractions, place the sealed capillary tubes in holder and place holder in oil bath.
8. Regulate transformer to give about one to two degrees rise in oil temperature per minute. Observe capillary tubes through magnifying glass and note temperature at which each set of crystals begins to deform. This temperature was recorded as the melting (or freezing) point of the solution.

To determine the accuracy of Equation 9, it was decided to test three substances of known molecular weight. The materials selected were of high molecular weight, corresponding to the expected molecular weight range of the asphalt fractions. The compounds were:

Name	Formula	Molecular Weight
Benzil (Dibenzoyl)	$(C_6H_5 \cdot CO)_2$	210.22
Diphenyl Mercury	$(C_6H_5)_2Hg$	354.81
Glyceryl Tristearate (Tristearin)	$(C_{17}H_{35}CO_2)_3C_3H_5$	891.45

Three determinations for each compound were made and the results obtained for each were within 4% of the tabulated molecular weight. (See Table 7)

From the above results, it was expected that the procedure would give consistent results within the same range of accuracy for the asphalt fractions.

Elasticity:

Elasticity determinations were made in the same apparatus developed by Buechley (3) and subsequently used by Miller (15) and Lamb (13).

The procedure was as follows:

1. Preparation of the samples consisted of heating the large storage can, in which the samples were received, in a 250°F oven until they became fluid. The samples were then stirred to insure uniformity of material and poured into 3-oz. cans for later use. Small cans were stored at room temperature for several days to minimize the effects of heating before further testing. (NOTE: The samples were not stored under a helium or nitrogen

environment, since this procedure would complicate the testing and any errors induced are believed to be within the range of experimental error.)

2. A 3-oz. sample was heated 45 minutes in the 270°F oven so that it was fluid enough for pouring.
3. The rotor and stator (Figure 7) were placed in the alignment fixture and heated with the sample for the last 15 minutes.
4. Viscometer and sample were removed from the oven and the molten asphalt was poured into the annulus. The stator was rotated slightly to insure complete filling. The lid was pressed into place and secured with machine screws and the apparatus was set aside to cool.
5. The amplifier and recorder were turned on at least one hour before a test to allow the circuit to stabilize prior to calibration.
6. Thirty minutes after the initial viscometer filling, the apparatus was positioned on its stand in the bath and thirty minutes more was allowed to reach thermal equilibrium with the bath. (Figure 8)
7. The stator shaft was rigidly attached to the torque-sensor by means of the metal sleeve. Slack was removed from the system by lightly pulling the bath handle until movement was observed on the amplifier needle.
8. The initial bath displacement scale reading was noted and a strain was imparted to the sample by quickly rotating the bath and latching the handle in place at a predetermined position. The exact strain rotation was determined as the difference between the final and initial readings on the

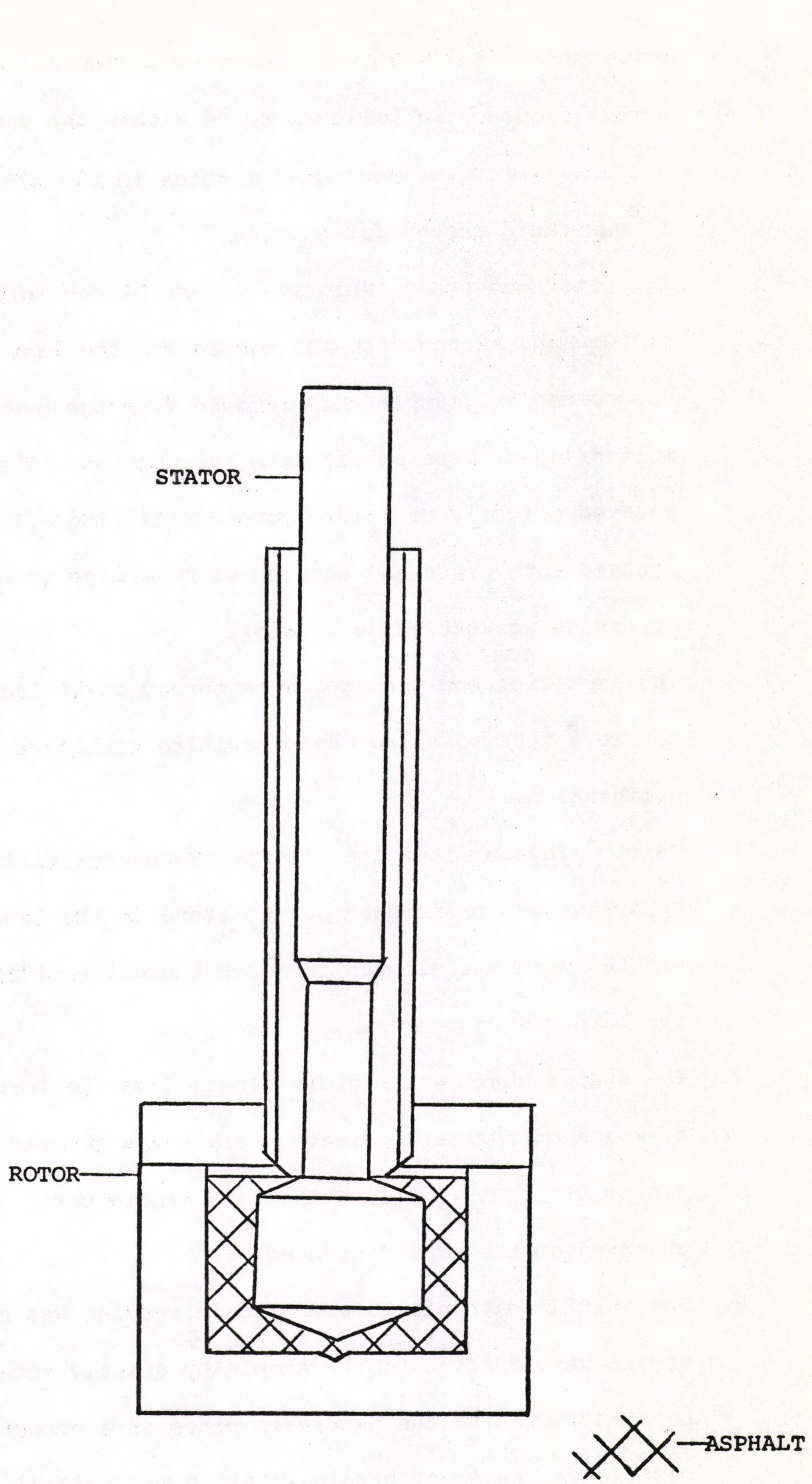

FIGURE 7 ROTATIONAL CONICYLINDRICAL VISCOMETER

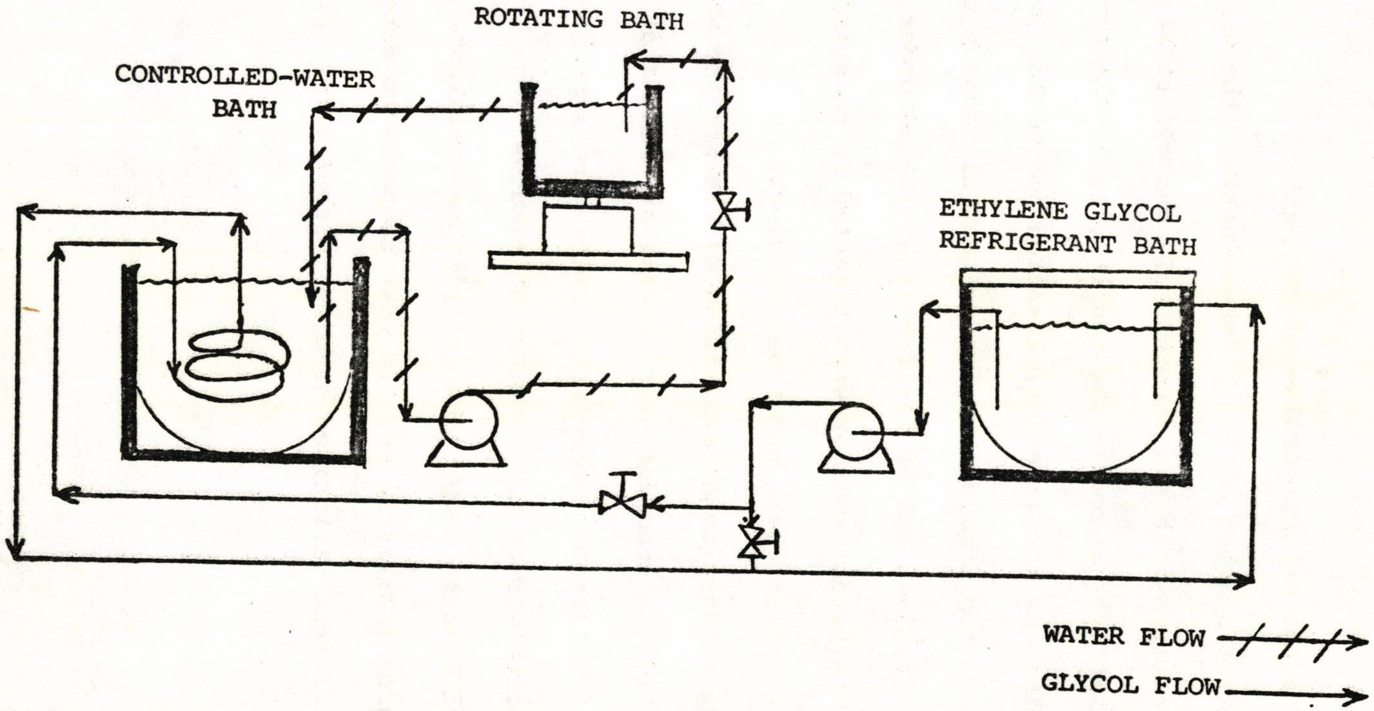

FIGURE 8 TEMPERATURE CONTROL SYSTEM FOR ELASTICITY MEASUREMENTS

arbitrary scale on the outside of the bath.

9. As the stress relaxed during a determination, the amplifier range-selector switch was successively changed to X1.0, X0.5, and X0.1 to increase the sensitivity of the recorded curve. Also, as the rate of relaxation decreased, chart speed was reduced from 25mm/sec to 5mm/sec and ultimately to 1mm/sec. This was due to the fact that the recorder needle displacement became smaller with time and by changing the chart speed, less chart paper was consumed.
10. The stress relaxation determination was terminated when the amplitude of the recorder trace became so small that the effects of noise and observation errors were significant. The time required was on the order of 45 minutes.

In all determinations except elasticity, three replicate samples were used. The three individual results were compared to determine if there were significant variations needing further trials for explanation.

PRESENTATION OF RESULTS

The final, calculated results only are presented in this report. The intermediate calculations, plots, and the original experimental data are recorded in bound laboratory notebooks and loose leaf binders in the Chemical Engineering Department of the University of Arkansas.

A generalized representation of G_r as a function of time is shown (Figure 10) since thirty-three separate plots were prepared during the course of this work and would be too cumbersome to include in the body of this report For the same reason, the plots of Absolute Viscosity as a function of Sample Age, Ductility as a function of Sample Age, and Penetration as a function of Sample Age are only shown in generalized form (Figures 11, 12, 13).

The equations resulting from the regression analysis are presented in Tables 1, 2, 3, 4, 5, and 6 along with standard deviations, standard errors of estimate, and multiple correlation coefficients. Since 114 equations were derived with multiple correlation coefficients (MCC) of 0.75 or higher, it was necessary to reduce this number somewhat so that the tables would not be cumbersome. For this reason, only those equations having a 0.90 or higher MCC are presented.

The results obtained in the determination of accuracy of the freezing-point depression method of molecular weight determination are presented in Table 7.

The distributions of composition fractions and their molecular weights as functions of sample age are shown in Figures 14 through 33.

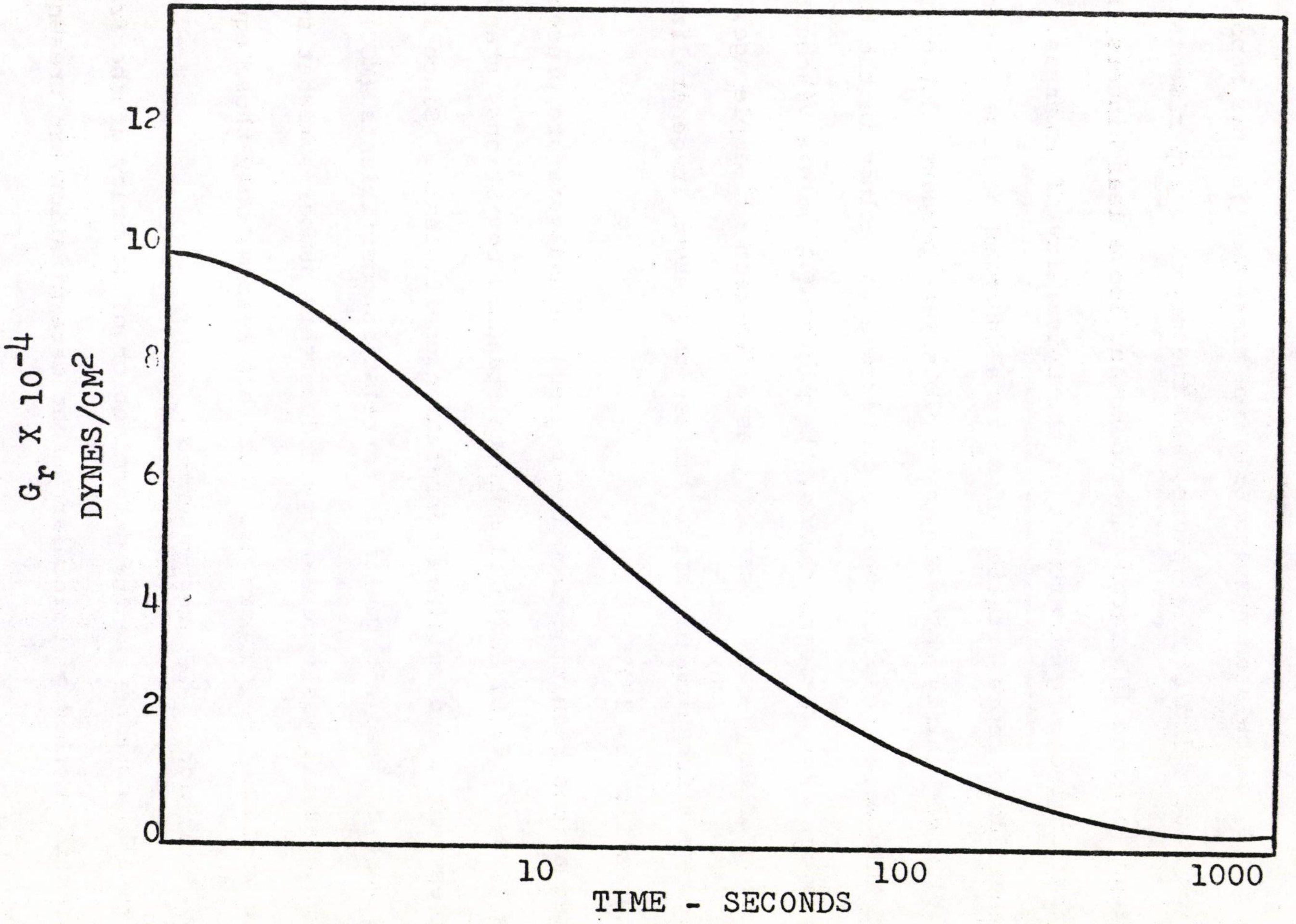

FIGURE 10. GENERALIZED REPRESENTATION, G_r vs T

AT 45 °F

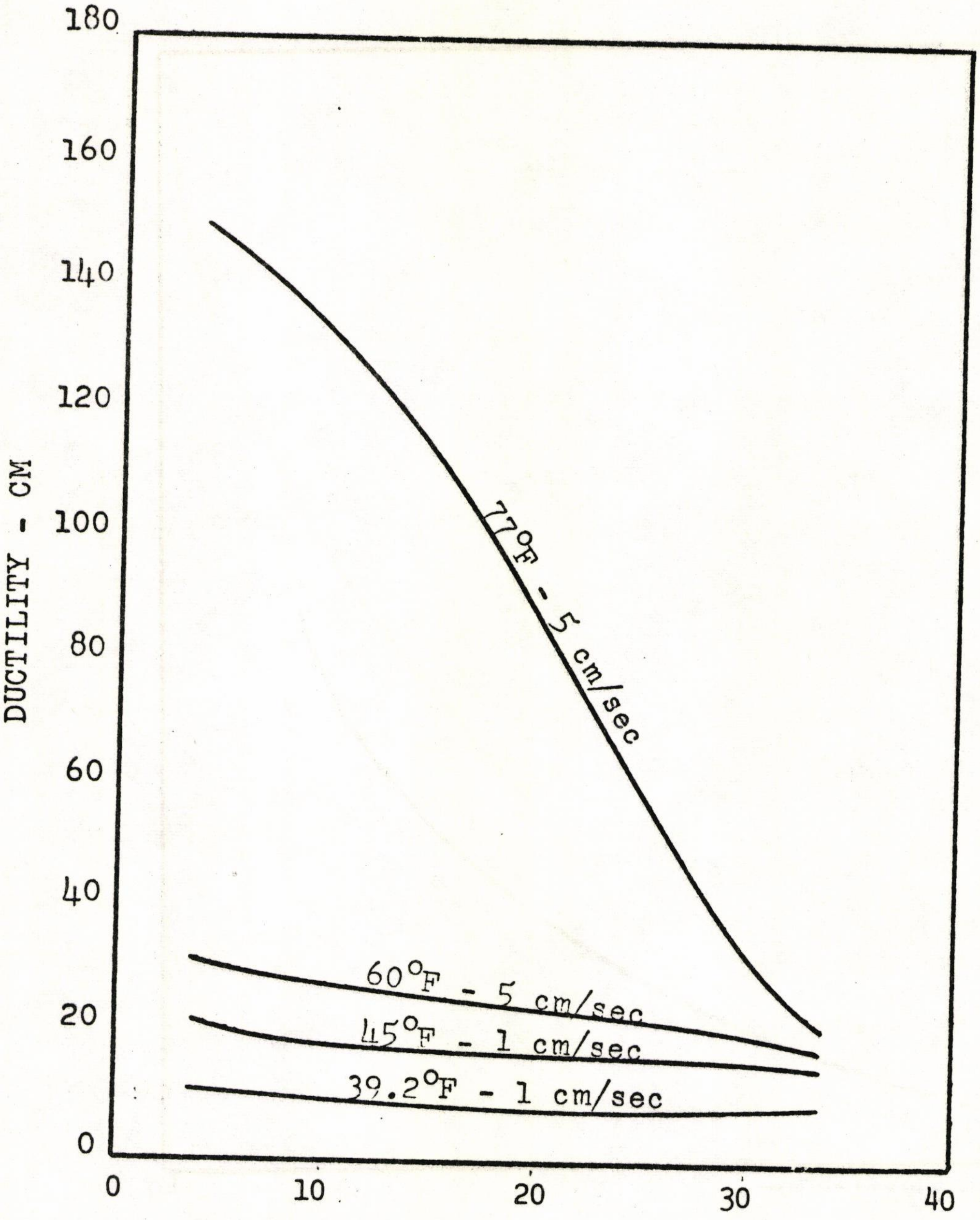

FIGURE 11. GENERALIZED REPRESENTATION,

DUCTILITY AS A FUNCTION OF SAMPLE AGE

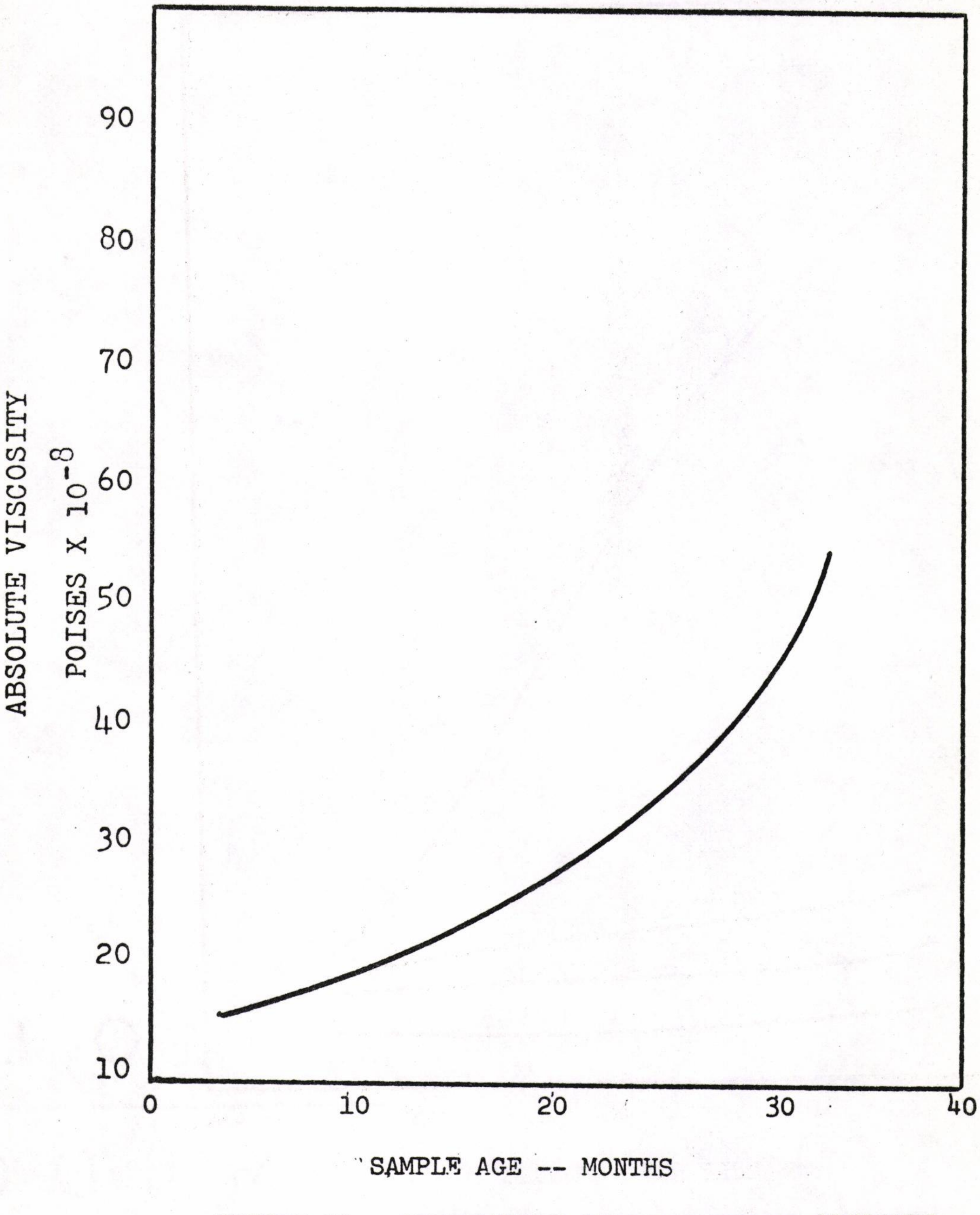

FIGURE 12. GENERALIZED REPRESENTATION, ABSOLUTE VISCOSITY AS A FUNCTION OF SAMPLE AGE AT 140 °F

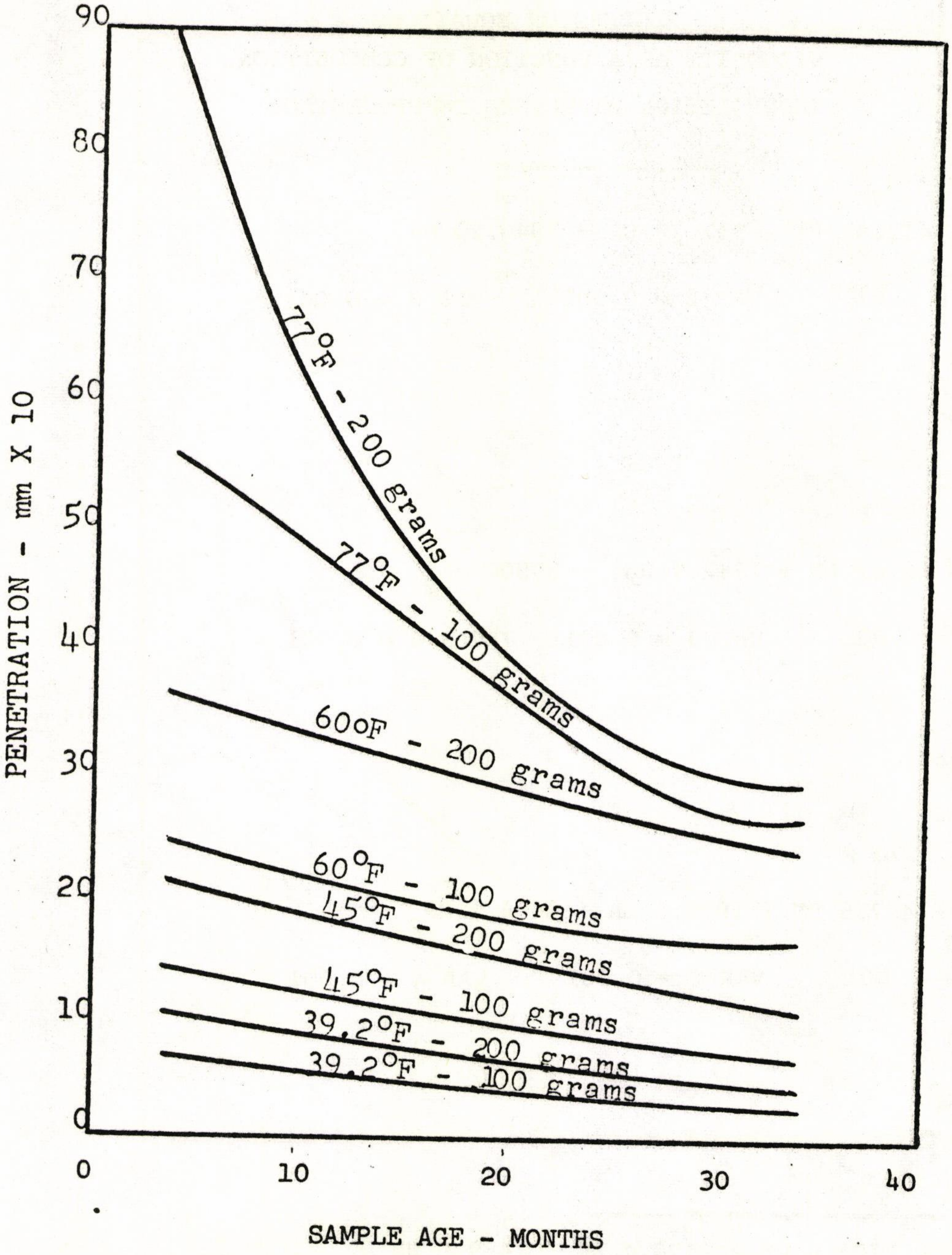

FIGURE 13. GENERALIZED REPRESENTATION, PENETRATION AS A FUNCTION OF SAMPLE AGE

TABLE 1

REGRESSION EQUATIONS
VISCOSITY AS A FUNCTION OF COMPOSITION
(COMPOSITION EXPRESSED IN PERCENTAGE)

C Samples, 270°F

$\mu = -3.61 + 412.91\ PN - 951.78\ LA + 2048.20\ HA_1$

s: VAR 1 = 0.011 VAR 2 = 0.001 VAR 3 = 0.001

S: 2779.3

MCC: 0.955

C Samples, 700°F

$\mu = 7223 - 521.1\ PN + 1712.7\ HA_1 - 59906\ HA_2$

s: VAR 1 = 0.001 VAR 3 = 0.001 VAR 4 = 0.001

S: 1679.1

MCC: 0.984

DM Samples, 270°F

$\mu = -78671 + 487.5\ PN + 1899.6\ LA + 9404.1\ HA_2$

s: VAR 1 = 0.001 VAR 2 = 0.001 VAR 4 = 0.001

S: 3276.1

MCC: 0.986

DM Samples, 700°F

$\mu = 158146 - 7705.8\ PN + 2490.4\ LA - 4459.6\ HX$

s: VAR 1 = 0.001 VAR 2 = 0.001 VAR 5 = 0.011

S: 4394.2

MCC: 0.976

TABLE I (Cont'd)

E Samples, 270°F

$\mu = 983.5 - 609.4\ PN - 13.19\ LA - 890.7\ HA_1 - 1617.0\ HA_2 + 2647.0\ HX$

s: VAR 1 = 0.001 VAR 2 = 0.001 VAR 3 = 0.001 VAR 4 = 0.001

VAR 5 = 0.001

S: 5097.3

MCC: 0.961

E Samples, 700°F

$\mu = 488699 - 3344.8\ PN - 6893.2\ LA - 5113.0\ HA_1 - 4917.5\ HA_2 - 2522.8\ HX$

s: VAR 1 = 0.001 VAR 2 = 0.001 VAR 3 = 0.001 VAR 4 = 0.001

VAR 5 = 0.011

S: 5876.6

MCC: 0.947

TABLE 2

REGRESSION EQUATIONS
VISCOSITY AS A FUNCTION OF
MOLECULAR WEIGHT FRACTIONS
(COMPOSITION TERMS EXPRESSED IN MOLECULAR WEIGHT OF EACH FRACTION)

C Samples, 300°F

$\mu = +51061 + 69.0\ LA - 69.5\ HA_1 - 10.1\ HX$

s: VAR 2 = 0.081 VAR 3 = 0.101 VAR 5 = 0.511

S: 1199.0

MCC: 0.992

C Samples, 700°F

$\mu = -16529 + 224.0\ PN - 26.5\ LA - 7.8\ HX$

s: VAR 1 = 0.021 VAR 2 = 0.081 VAR 5 = 0.481

S: 1893.3

MCC: 0.979

TABLE 3

REGRESSION EQUATIONS

DUCTILITY AS A FUNCTION OF COMPOSITION

(COMPOSITION EXPRESSED IN PERCENTAGES)

B Samples, 270°F, 39.2/1

$\text{Duct} = 40.7 - 0.36\ PN - 0.52\ LA - 0.37\ HA_1 + 0.17\ HA_2 - 0.22\ HX$

s: VAR 1 = 0.061 VAR 2 = 0.041 VAR 3 = 0.021 VAR 4 = 0.011 VAR 5 = 0.031

S: 0.493

MCC: 0.928

DL Samples, 270°F, 45/1

$\text{Duct} = -16.0 + 0.2PN + 0.3LA + 0.1HA_1 + 0.3HA_2 + 0.2HX$

s: VAR 1 = 3.211 VAR 2 = 3.401 VAR 3 = 3.951 VAR 4 = 1.451 VAR 5 = 3.161

S: 0.233

MCC: 0.980

DL Samples, 700°F, 45/1

$\text{Duct} = 1.8 - 0.2PN + 0.1LA + 0.1\ HA_2 + 0.1HX$

s: VAR 1 = 3.111 VAR 2 = 2.201 VAR 4 = 1.291 VAR 5 = 4.641

S: 0.273

MCC: 0.973

TABLE 3 (Cont'd)

DM Samples, 270°F, 45/5

$\mathrm{Duct} = -22.5 + 0.5\mathrm{PN} + 0.4\mathrm{HA}_1 + 0.4\mathrm{HX}$

s: VAR 1 = 1.801 VAR 3 = 4.471 VAR 5 = 3.571

S: 0.409

MCC: 0.948

DM Samples, 270°F, 45/1

$\mathrm{Duct} = 2.4 - 0.2\mathrm{PN} + 0.2\mathrm{LA} - 0.1\mathrm{HA}_2$

s: VAR 1 = 1.801 VAR 2 = 2.861 VAR 4 = 1.581

S: 0.251

MCC: 0.957

DM Samples, 700°F, 60/5

$\mathrm{Duct} = 5.6 + 0.5\mathrm{PN} - 0.1\mathrm{HA}_1 - 0.2\mathrm{HX}$

s: VAR 1 = 3.471 VAR 3 = 4.671 VAR 5 = 5.081

S: 0.195

MCC: 0.999

DM Samples, 700°F, 45/5

$\mathrm{Duct} = -6.8 + 0.2\mathrm{PN} + 0.2\mathrm{HA}_1 + 0.1\mathrm{HX}$

s: VAR 1 = 3.471 VAR 3 = 4.671 VAR 5 = 5.081

S: -.246

MCC: 0.982

TABLE 3 (Cont'd)

E Samples, 270°F, 77/5

$Duct = 50.1 + 0.3PN - 0.3LA + 1.4HA_1 + 2.1HA_2 - 2.4HX$

s: VAR 1 = 3.291 VAR 2 = 3.741 VAR 3 = 3.011 VAR 4 = 1.091 VAR 5 = 3.731

S: 7.468

MCC: 0.945

E Samples, 700°F, 77/5

$Duct = 491.5 + 4.7PN + 7.1LA + 5.8HA_1 + 5.6HA_2 + 2.9HX$

s: VAR 1 = 3.281 VAR 2 = 3.171 VAR 3 = 4.161 VAR 4 = 2.081 VAR 5 = 6.181

S: 7.544

MCC: 0.944

E Samples, 700°F, 45/5

$Duct = 1.2 - 0.1PN + 0.2LA - 0.4HA_2$

s: VAR 1 = 3.541 VAR 2 = 2.841 VAR 4 = 1.781

S: 0.543

MCC: 0.956

E Samples, 700°F, 45/1

$Duct = 10.0 - 0.2PN - 0.1LA - 0.1HA_1 - 0.3HA_2 - 0.1HX$

s: VAR 1 = 3.571 VAR 2 = 3.011 VAR 3 = 3.991 VAR 4 = 1.971 VAR 5 = 5.781

S: 0.313

MCC: 0.978

TABLE 4

REGRESSION EQUATIONS

DUCTILITY AS A FUNCTION OF MOLECULAR WEIGHT FRACTION

(COMPOSITION TERMS EXPRESSED IN MOLECULAR WEIGHT OF EACH FRACTION)

A Samples, 300°F, 60/5

$\text{Duct} = 15.71 + 0.05\text{PN} - 0.03\text{LA} + 0.03\text{HA}_1 - 0.02\text{HA}_2 + 0.003\text{H}^{\text{X}}$

s: VAR 1 = 67.621 VAR 2 = 105.781 VAR 3 = 90.341 VAR 4 = 138.881

VAR 5 = 1172.841

S: 6.472

MCC: 0.902

DM Samples, 300°F, 77/5

$\text{Duct} = 648.6 + 0.5\text{PN} + 0.4\text{HA}_1 + 0.4\text{HA}_2$

s: VAR 1 = 58.771 VAR 3 = 91.871 VAR 4 = 95.331

S: 26.705

MCC: 0.902

DM Samples, 300°F, 60/5

$\text{Duct} = -52.5 + 0.05\text{PN} + 0.04\text{HA}_2 + 0.003\text{HX}$

s: VAR 1 = 58.771 VAR 4 = 95.331 VAR 5 = 945.261

S: 1.306

MCC: 0.922

DM Samples, 300°F, 45/5

$\text{Duct} = 358.2 + 0.7\text{LA} + 0.7\text{HA}_1 - 1.4\text{HA}_2$

s: VAR 2 = 80.441 VAR 3 = 54.241 VAR 4 = 43.501

S: 10.681

MCC: 0.985

TABLE 4 (Cont'd)

DM Samples, 300°F, 45/1

Duct = $-0.04 + 0.003PN + 0.003LA + 0.001HA_1$

s: VAR 1 = 58.771 VAR 2 = 95.541 VAR 3 = 91.871

S: 0.254

MCC: 0.956

DM Samples, 700°F, 77/5

Duct = $358.2 + 0.7LA + 0.7HA_1 - 1.4HA_2$

s: VAR 2 = 80.441 VAR 3 = 54.241 VAR 4 = 43.501

S: 10.681

MCC: 0.985

DM Samples, 700°F, 45/5

Duct = $9.7 - 0.02PN - 0.01HA_1 + 0.009HA_2$

s: VAR 1 = 36.871 VAR 3 = 54.241 VAR 4 = 43.501

S: 0.133

MCC: 0.995

E Samples, 300°F, 77/5

Duct = $-8.8 - 0.3PN + 0.1LA + 0.03HA_1 - 0.02HA_2 + 0.03HX$

s: VAR 1 = 47.051 VAR 2 = 81.871 VAR 3 = 104.651 VAR 4 = 90.611

VAR 5 = 579.161

S: 10.138

MCC: 0.918

TABLE 4 (Cont'd)

E Samples, 700°F, 45/5

Duct = $5.0 - 0.02HA_1 + 0.01\ HA_2 + 0.001HX$

s: VAR 3 = 77.191 VAR 4 = 47.291 VAR 5 611.681

S: 0.602

MCC: 0.946

TABLE 5

REGRESSION EQUATIONS
PENETRATION AS A FUNCTION OF COMPOSITION
(COMPOSITION EXPRESSED IN PERCENTAGE)

A Samples, 270°F, 77/200

$PEN = 91.5 + 2.3PN + 2.4LA + 2.7HA_1 - 6.5HA_2 + 1.5HX$

s: VAR 1 = 7.781 VAR 2 = 5.061 VAR 3 = 3.101 VAR 4 = 0.841

VAR 5 = 3.601

S: 2.911

MCC: 0.902

A Samples, 270°F, 60/100

$PEN = 16.1 + 0.6PN + 0.5LA + 0.7HA_1 - 2.0HA_2 + 0.3HX$

s: VAR 1 = 7.781 VAR 2 = 5.061 VAR 3 = 3.101 VAR 4 = 0.841

VAR 5 = 3.601

S: 0.823

MCC: 0.933

A Samples, 700°F, 77/100

$PEN = 128.8 - 1.2PN - 1.0LA - 0.6HA_1 - 0.005HA_2$

s: VAR 1 = 2.951 VAR 2 = 4.871 VAR 3 = 4.011 VAR 4 1.941

s: 1.052

MCC: 0.946

B. Samples, 270°F, 39.2/100

$PEN = 22.9 + 0.15PN - 0.23LA - 0.34HA_1 - 0.52HA_2 - 0.16HX$

s: VAR 1 = 5.591 VAR 2 = 3.591 VAR 3 = 1.921 VAR 4 = 0.711

TABLE 5 (Cont'd)

VAR 5 = 3.141

S: 1.003

MCC: 0.932

B Samples, 700°F, 60/100

$PEN = 50.5 + 0.3PN - 0.5LA - 0.6HA_1 - 0.5HA_2 - 0.1HX$

s: VAR 1 = 15.521 VAR 2 = 29.981 VAR 3 = 26.691 VAR 4 = 6.741

VAR 5 = 18.591

S: 1.187

MCC: 0.904

DL Samples, 270°F, 45/200

$PEN = 11.6 + 0.15PN - 0.20LA - 0.15HA_1 + 0.15HA_2 + 0.35HX$

s: VAR 1 = 3.211 VAR 2 = 3.401 VAR 3 = 3.751 VAR 4 1.451

VAR 5 = 3.161

S: 1.557

MCC: 0.913

E Samples, 270°F, 60/200

$PEN = 28.7 - 0.2PN - 0.3LA - 0.1HA_1 - 1.0HA_2 - 0.5HX$

s: VAR 1 = 3.291 VAR 2 = 4.031 VAR 3 = 2.941 VAR 4 = 1.081

VAR 5 = 3.281

S: 1.220

MCC: 0.997

TABLE 5 (Cont'd)

E Samples, 700°F, 60/100

$PEN = 10.4 - 0.4PN + 0.3LA - 0.04HA_1 - 0.2HA_2 + 0.02HX$

s: VAR 1 = 3.141 VAR 2 = 3.131 VAR 3 = 3.571 VAR 4 = 2.111

VAR 5 = 4.991

S: 1.457

MCC: 0.918

E Samples, 700°F, 60/200

$PEN = 601.6 - 8.03PN - 5.83LA - 6.85HA_1 - 9.65HA_2 - 3.61HX$

s: VAR 1 = 3.141 VAR 2 = 3.131 VAR 3 = 3.571 VAR 4 2.111

VAR 5 = 4.991

S: 5.241

MCC: 0.950

TABLE 6

REGRESSION EQUATIONS
PENETRATION AS A FUNCTION OF MOLECULAR WEIGHT FRACTION
(COMPOSITION TERM EXPRESSED IN MOLECULAR WEIGHT OF EACH FRACTION)

B Samples, 700°F, 77/200

$PEN = 145.4 - 0.20PN - 0.01LA + 0.01HA_1 - 0.01HA_2 - 0.005HX$

s: VAR 1 = 47.381 VAR 2 = 85.441 VAR 3 = 55.101 VAR 4 = 97.081

VAR 5 = 1053.171

S: 4.820

MCC: 0.905

B Samples, 700°F, 60/100

$PEN = -2.9 - 0.012PN + 0.006LA + 0.03HA_1 + 0.006HA_2 - 0.0002HX$

s: VAR 1 = 47.381 VAR 2 = 85.441 VAR 3 = 55.101 VAR 4 = 97.081

VAR 5 = 1053.171

S: 0.713

MCC: 0.966

B Samples, 700°F, 60/200

$PEN = 5.4 - 0.01PN + 0.01LA + 0.03HA_1 + 0.0007HA_2 - 0.00004HX$

s: VAR 1 = 47.381 VAR 2 = 85.441 VAR 3 = 55.101 VAR 4 = 97.081

VAR 5 = 1053.171

S: 1.349

MCC: 0.926

E Samples, 300°F, 60/200

$PEN = -36.4 + 0.06PN + 0.05LA - 0.01HA_1 + 0.002HA_2 + 0.015HX$

TABLE 6 (Cont'd)

s: VAR 1 = 50.921 VAR 2 = 95.391 VAR 3 = 105.511 VAR 4 = 97.641

VAR 5 = 464.011

S: 5.141

MCC: 0.952

E. Samples, 700°F, 77/100

$PEN = 26.4 - 0.02PN + 0.06LA - 0.04HA_1 + 0.002HA_2 + 0.004HX$

s: VAR 1 = 54.701 VAR 2 = 64.831 VAR 3 = 86.911 VAR 4 = 72.761

VAR 5 = 639.441

S: 2.972

MCC: 0.942

E Samples, 700°F, 77/200

$PEN = 45.2 - 0.03PN + 0.08LA - 0.06HA_1 + 0.006HA_2 + 0.004HX$

s: VAR 1 = 54.701 VAR 2 = 64.831 VAR 3 = 86.911 VAR 4 = 72.761

VAR 5 = 639.441

S: 5.088

MCC: 0.909

TABLE 7

MOLECULAR WEIGHT DETERMINATION

ACCURACY TEST OF APPARATUS

Sample	Actual Molecular Weight	Experimental Molecular Weight	% - Error
Benzil (1)	210.22	211.00	0.37
Benzil (2)	210.22	217.91	3.65
Benzil (3)	210.22	210.44	0.10
Diphenyl-Hg (1)	354.81	364.65	2.77
Diphenyl-Hg (2)	354.81	365.75	3.08
Diphenyl-Hg (3)	354.81	355.53	0.20
Glycerly Tristearate (1)	891.45	858.07	3.74
Glyceryl Tristearate (2)	891.45	923.16	3.56
Glyceryl Tristearate (3)	891.45	922.75	3.51

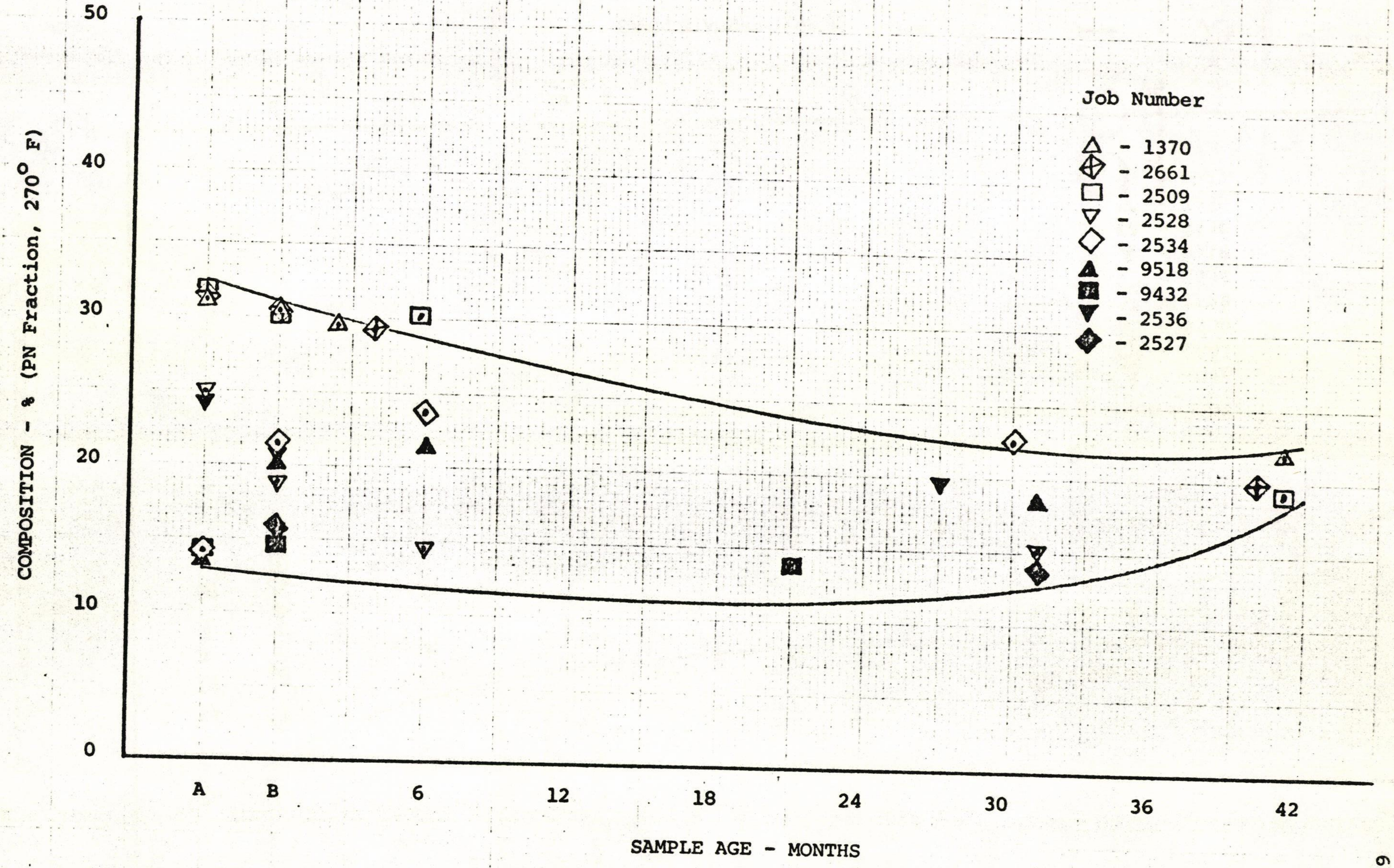

Figure 14. Composition as a function of Sample Age (PN Fraction, 270° F)

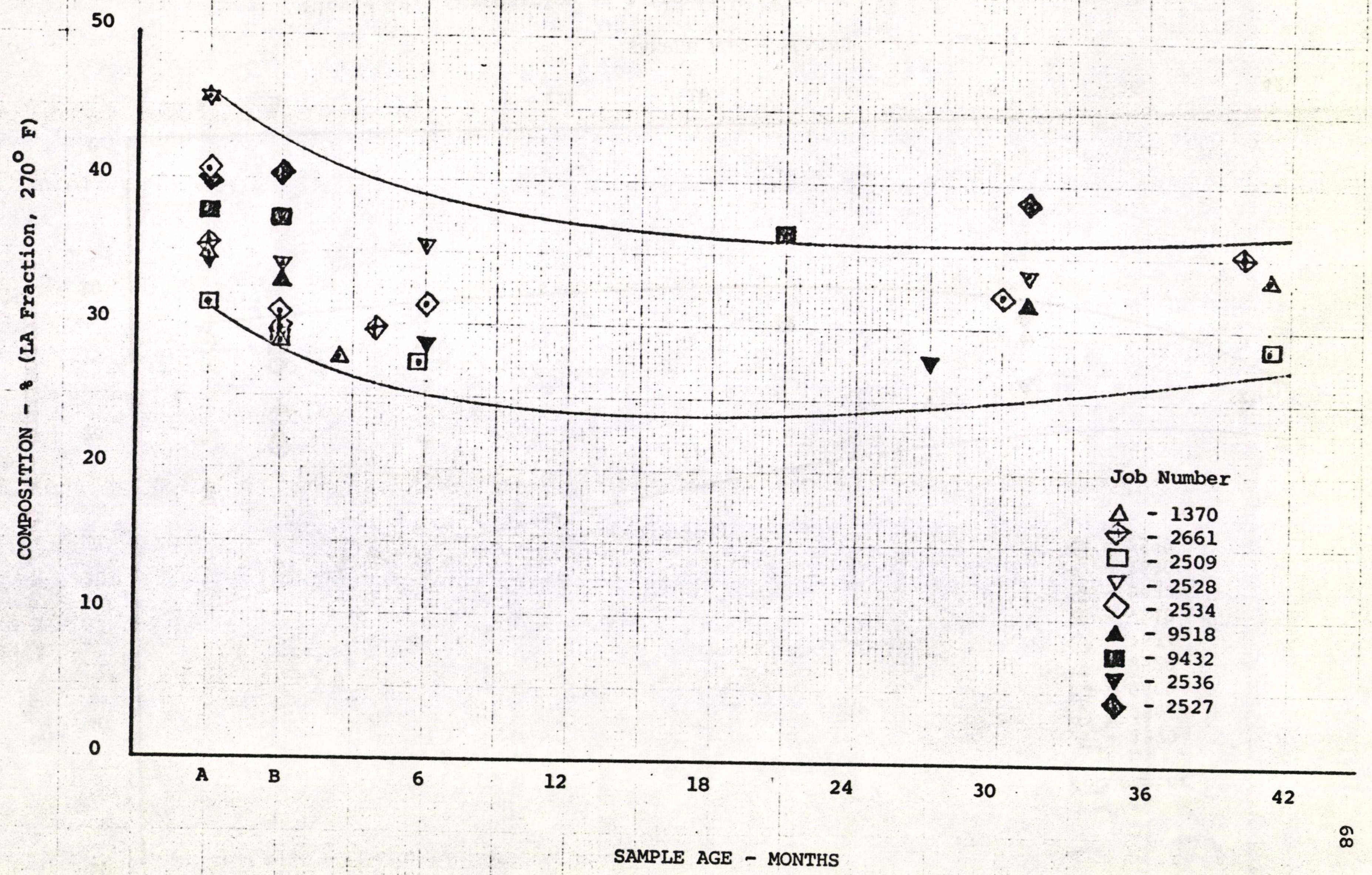

Figure 15. Composition as a function of Sample Age (LA Fraction, 270° F)

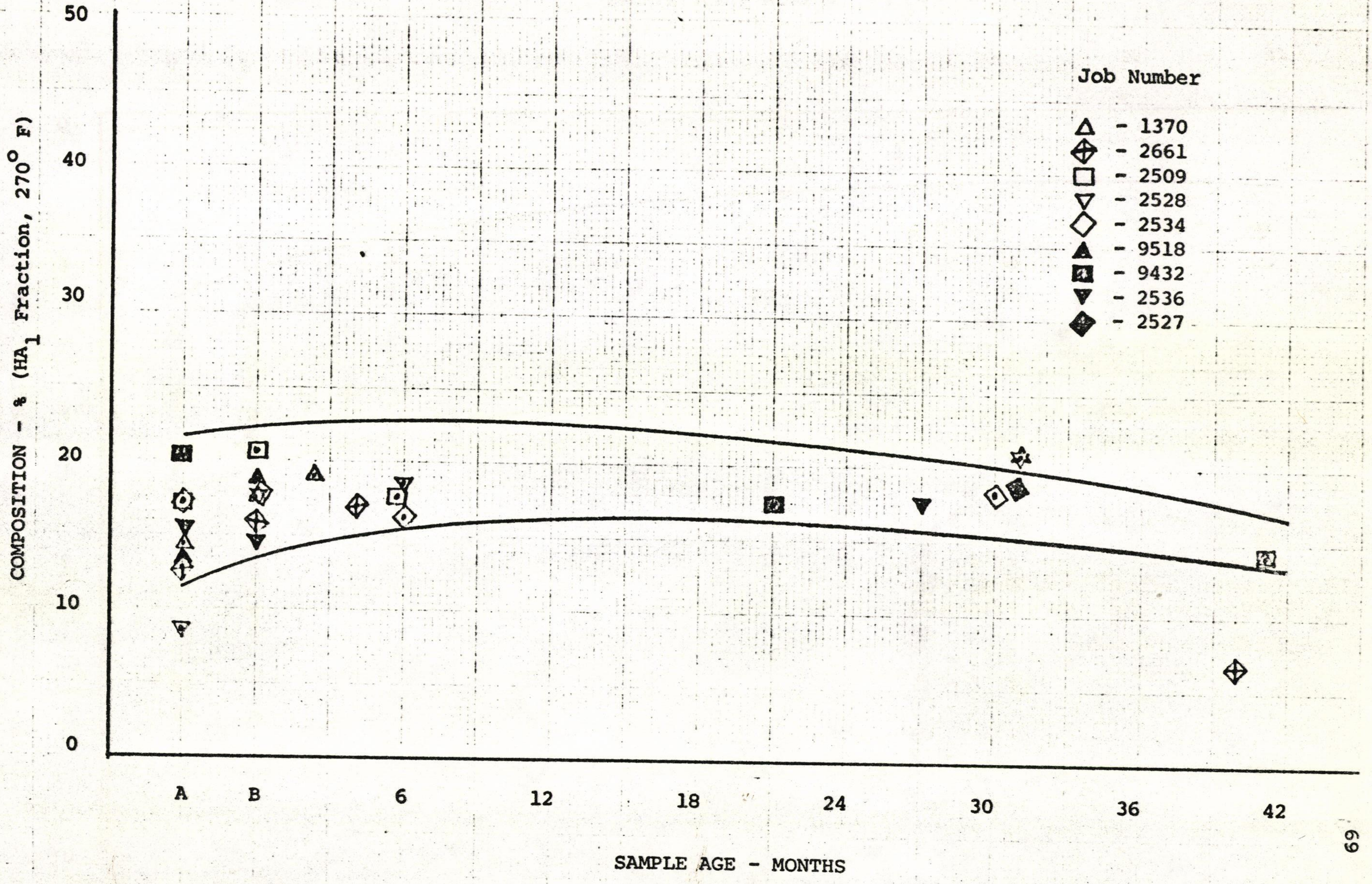

Figure 16. Composition as a function of Sample Age (HA_1 Fraction, 270° F)

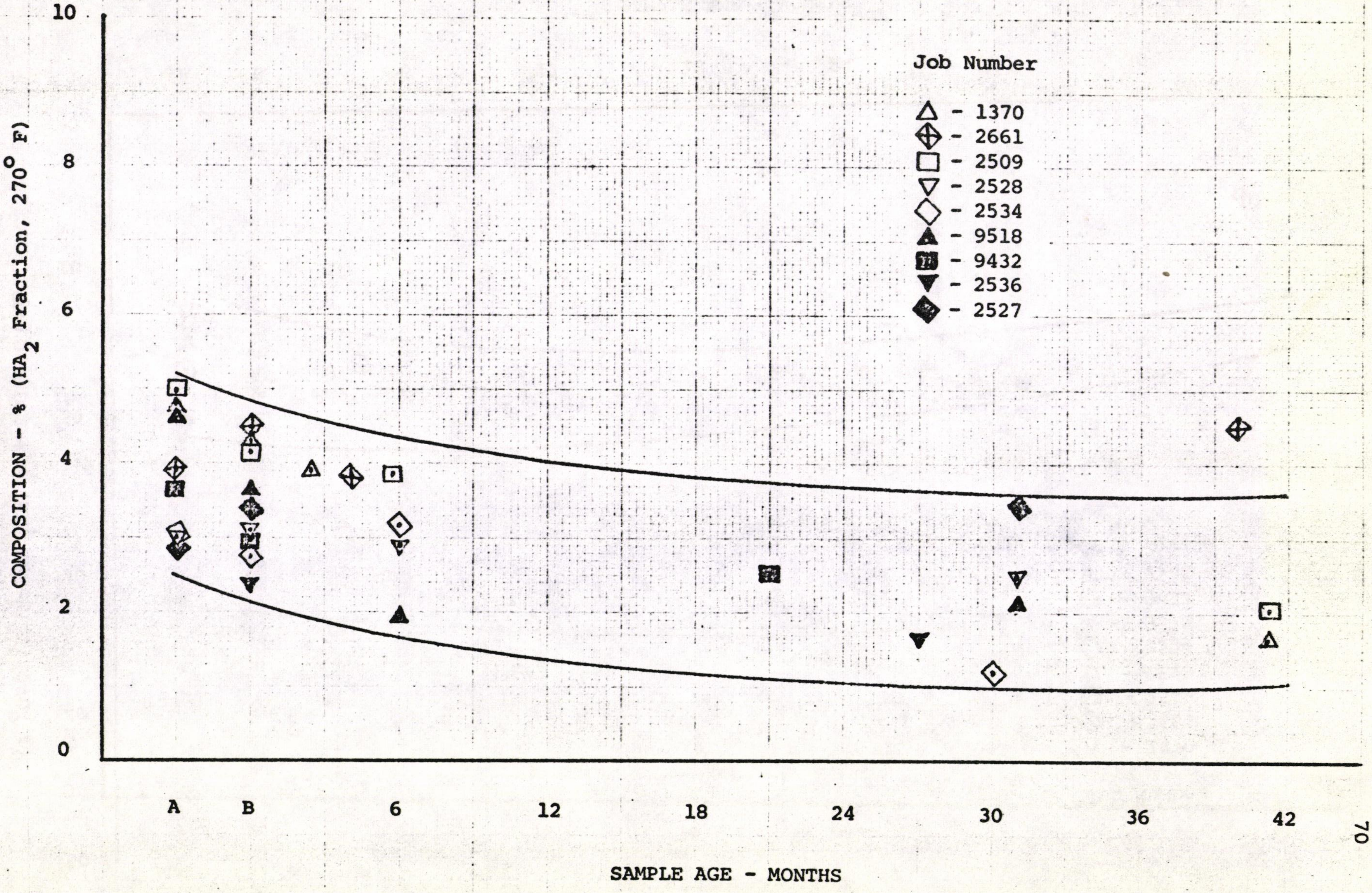

Figure 17. Composition as a function of Sample Age (HA$_2$ Fraction, 270° F)

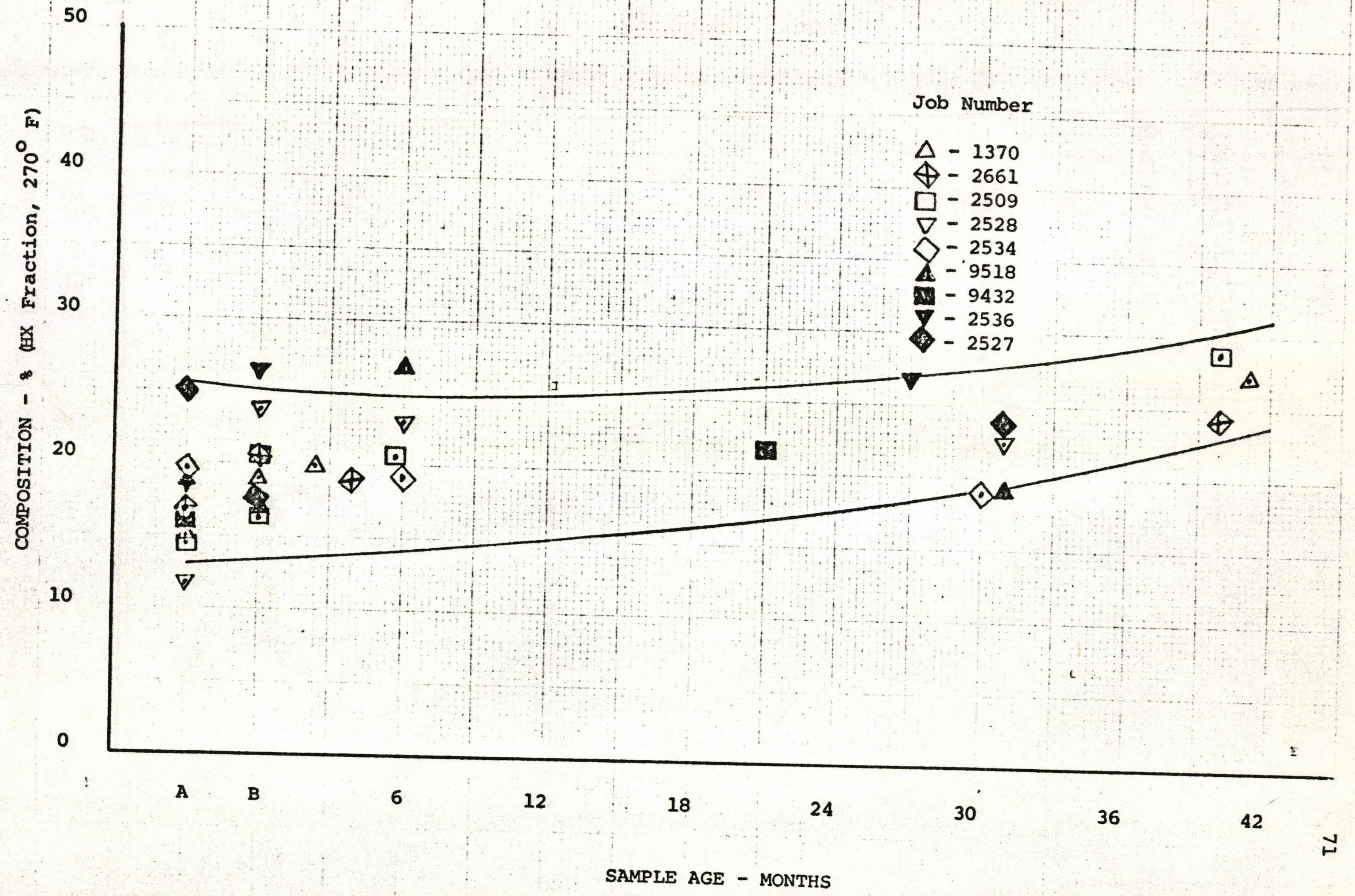

Figure 18. Composition as a function of Sample Age (HX Fraction, 270° F)

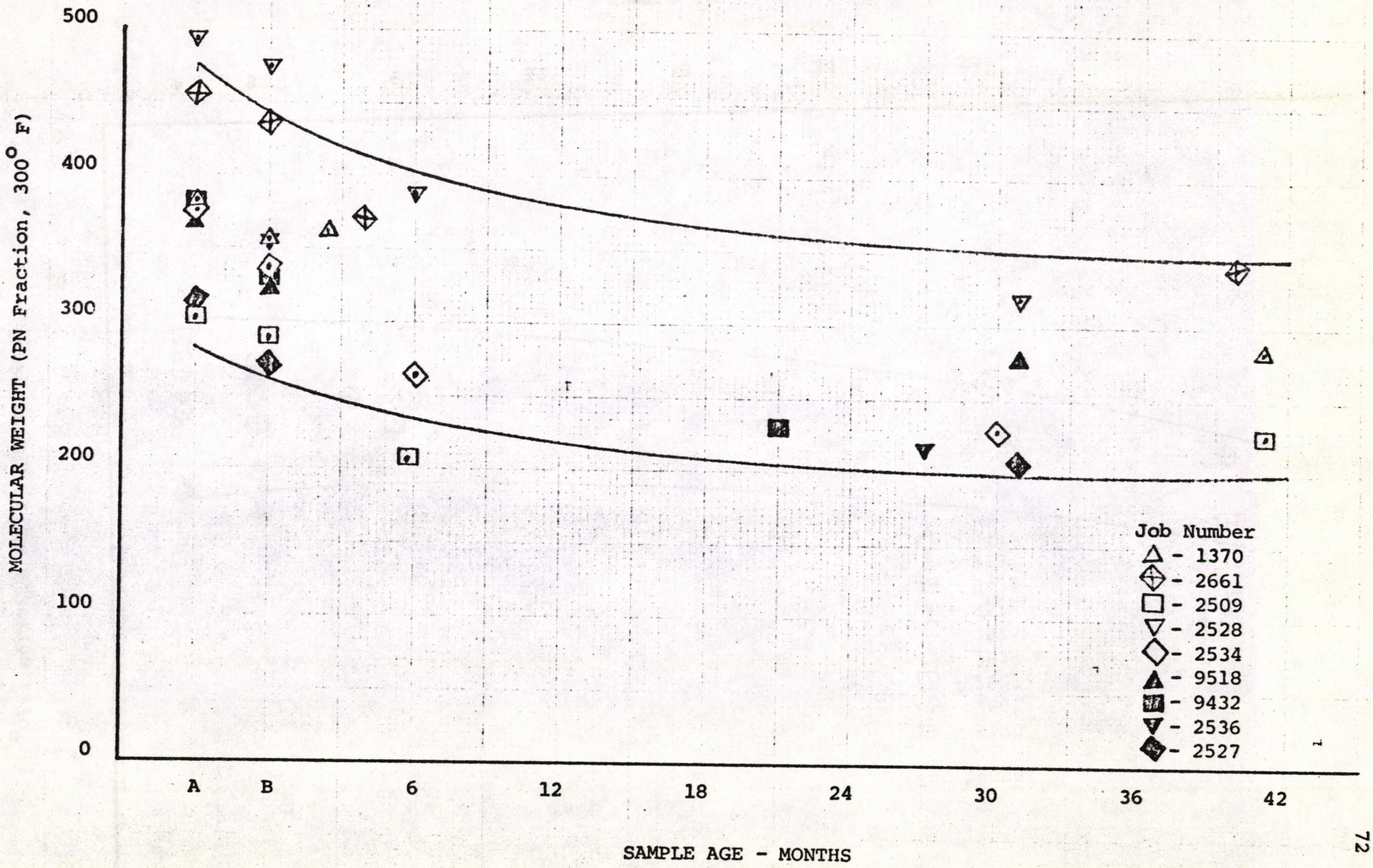

Figure 19. Molecular Weight as a function of Sample Age (PN Fraction, 300° F)

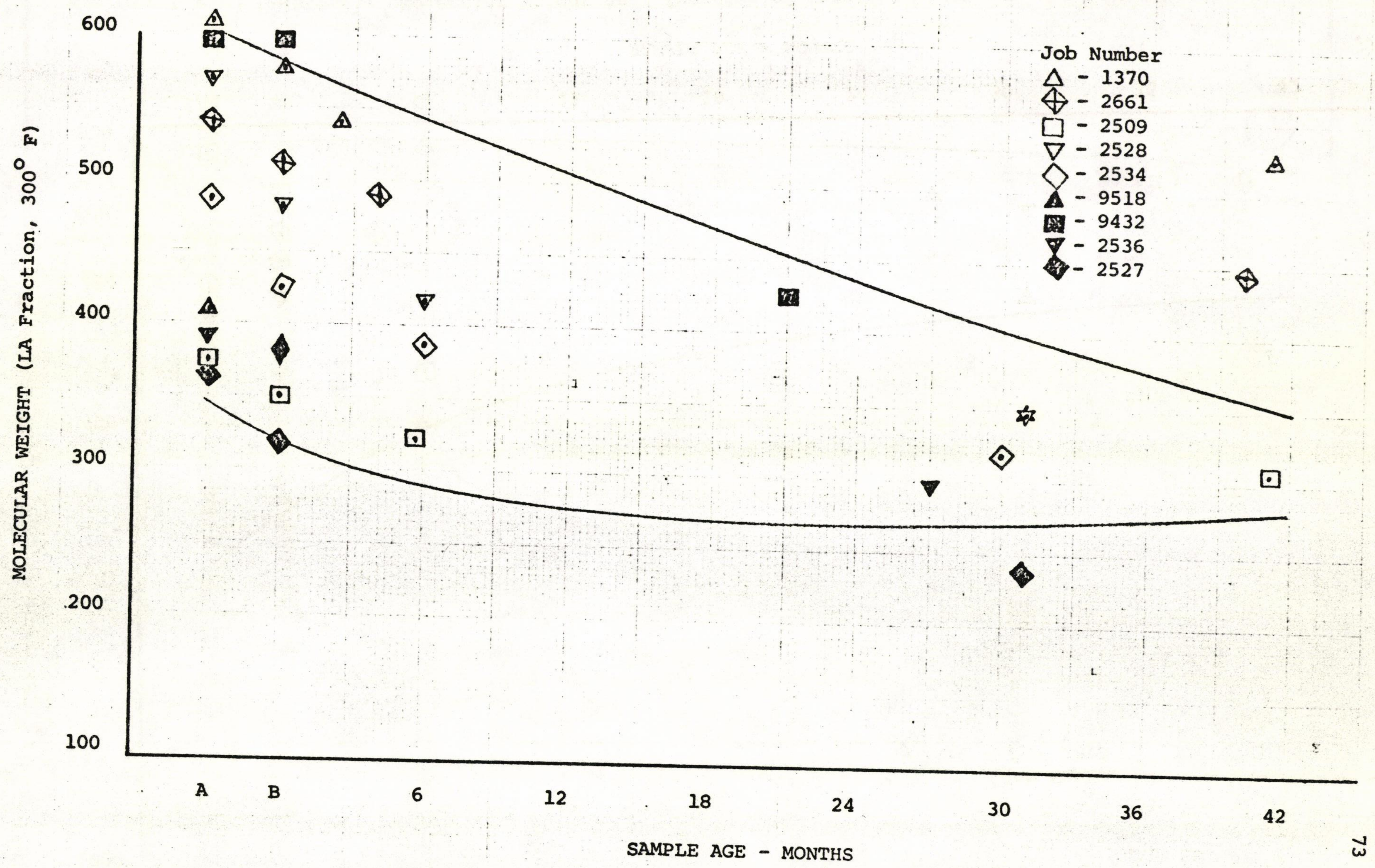

Figure 20. Molecular Weight as a function of Sample Age (LA Fraction, 300° F)

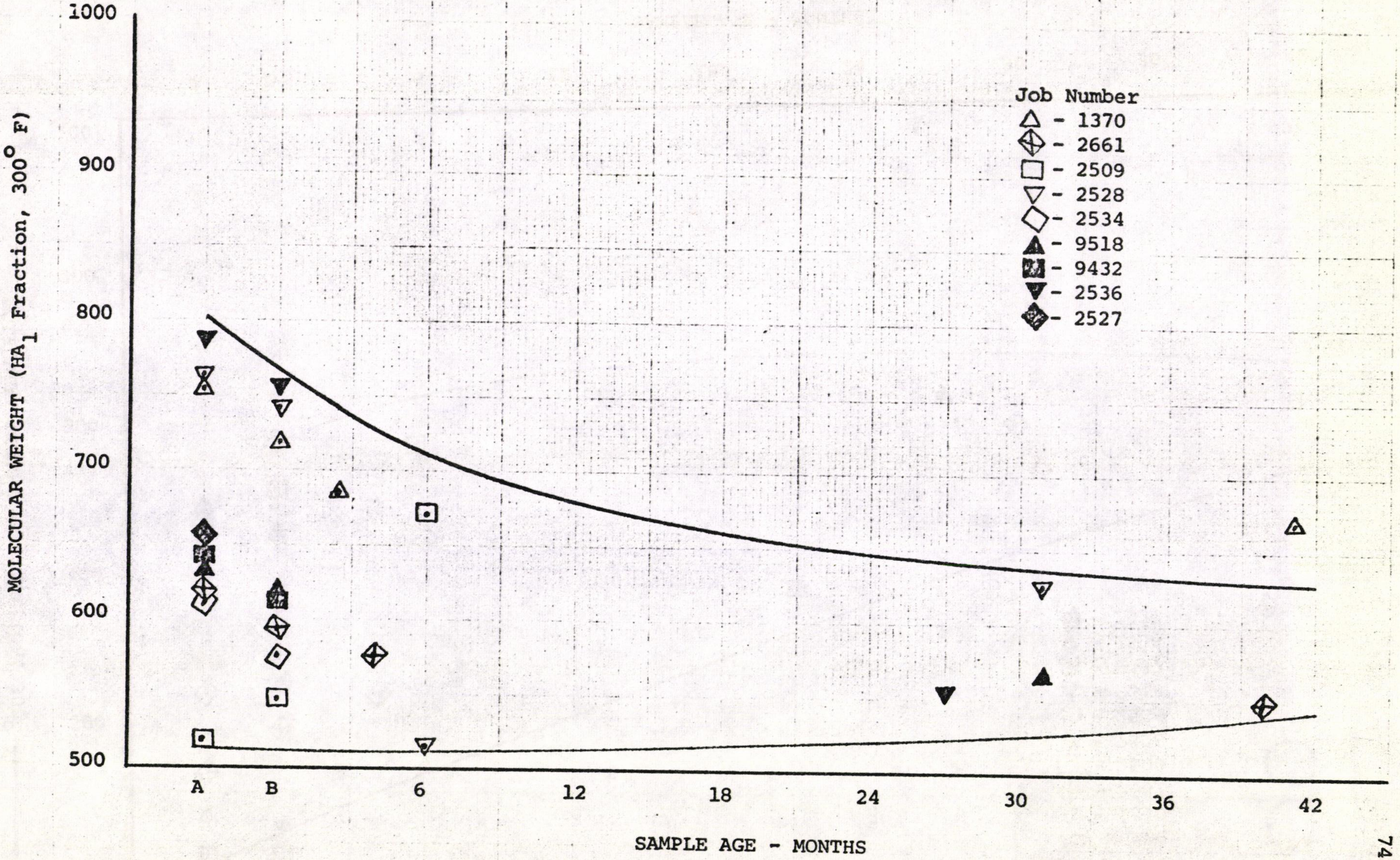

Figure 21. Molecular Weight as a function of Sample Age (HA_1 Fraction, 300° F)

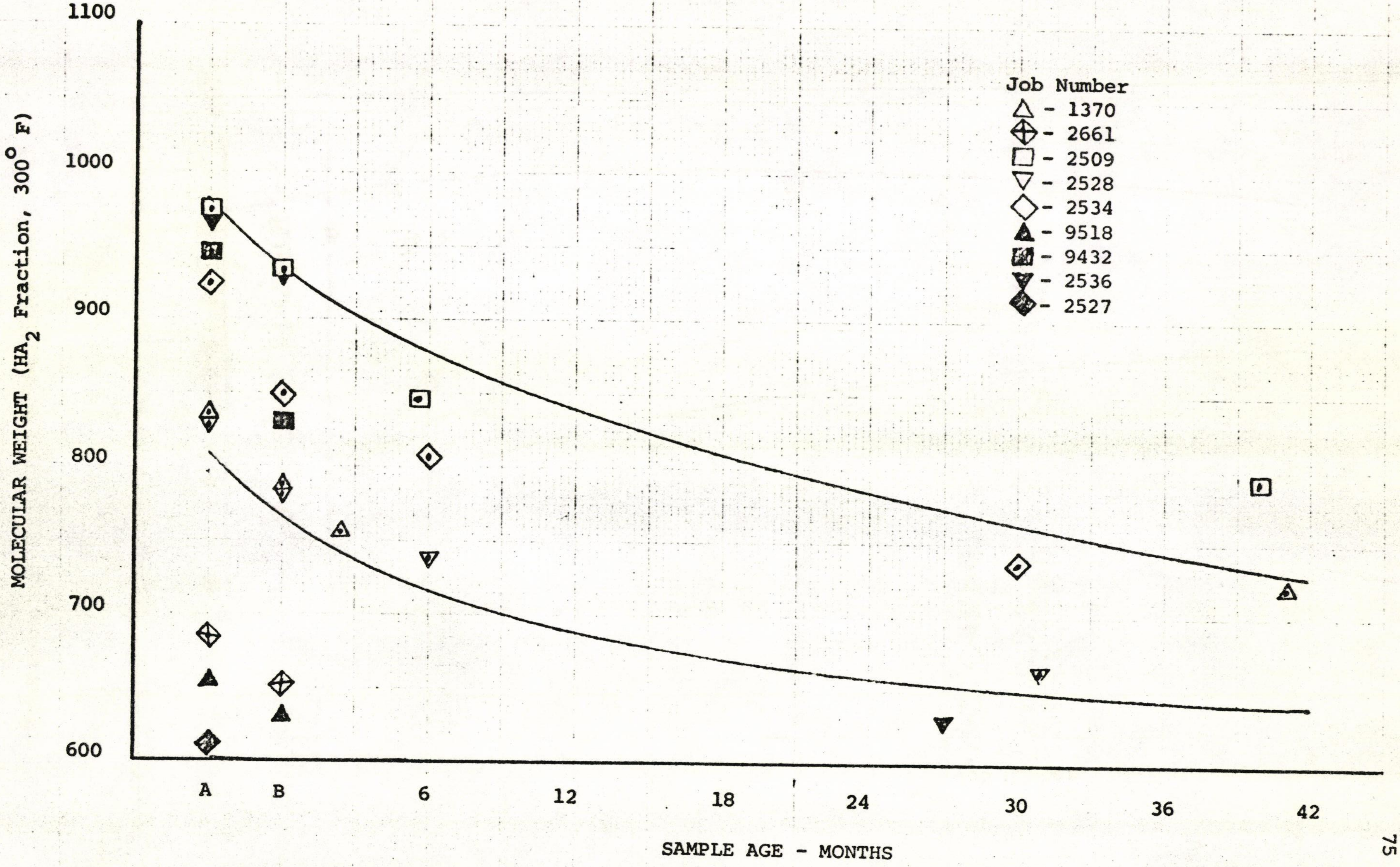

Figure 22. Molecular Weight as a function of Sample Age (HA$_2$ Fraction, 300° F)

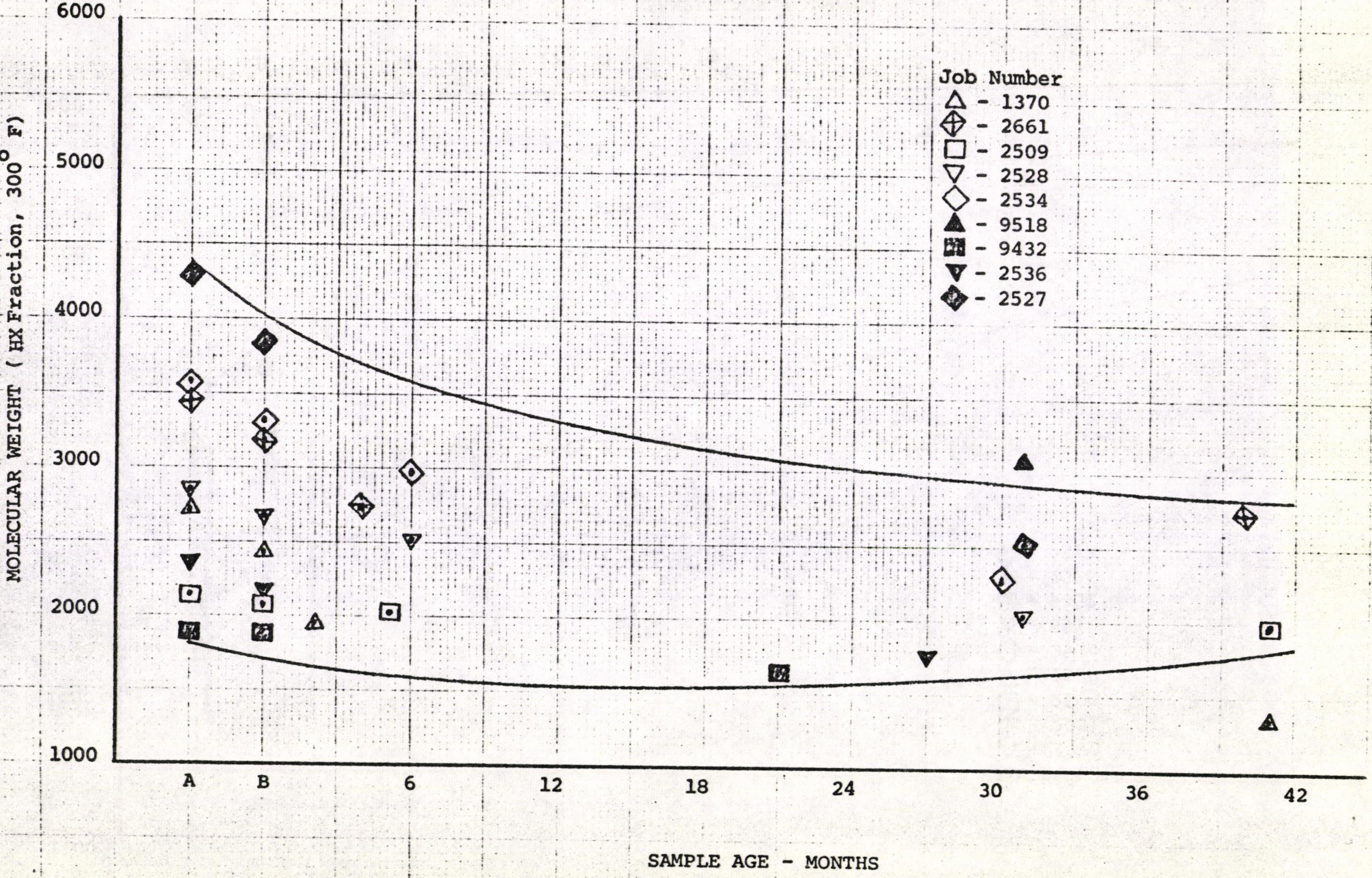

Figure 23. Molecular Weight as a function of Sample Age (HX Fraction, 300° F)

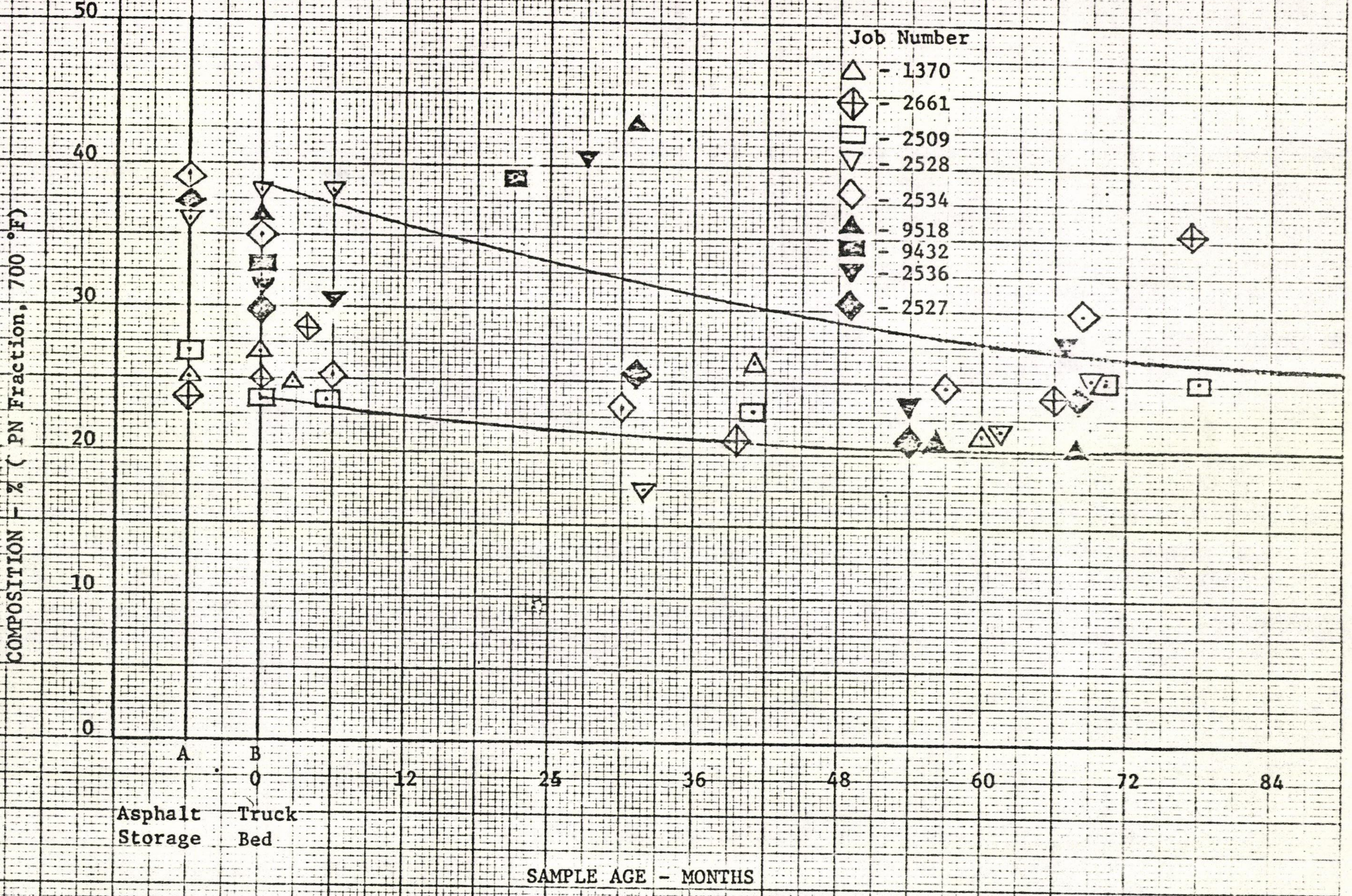

Figure 24. Composition as a function of Sample Age (PN Fraction, 700 °F)

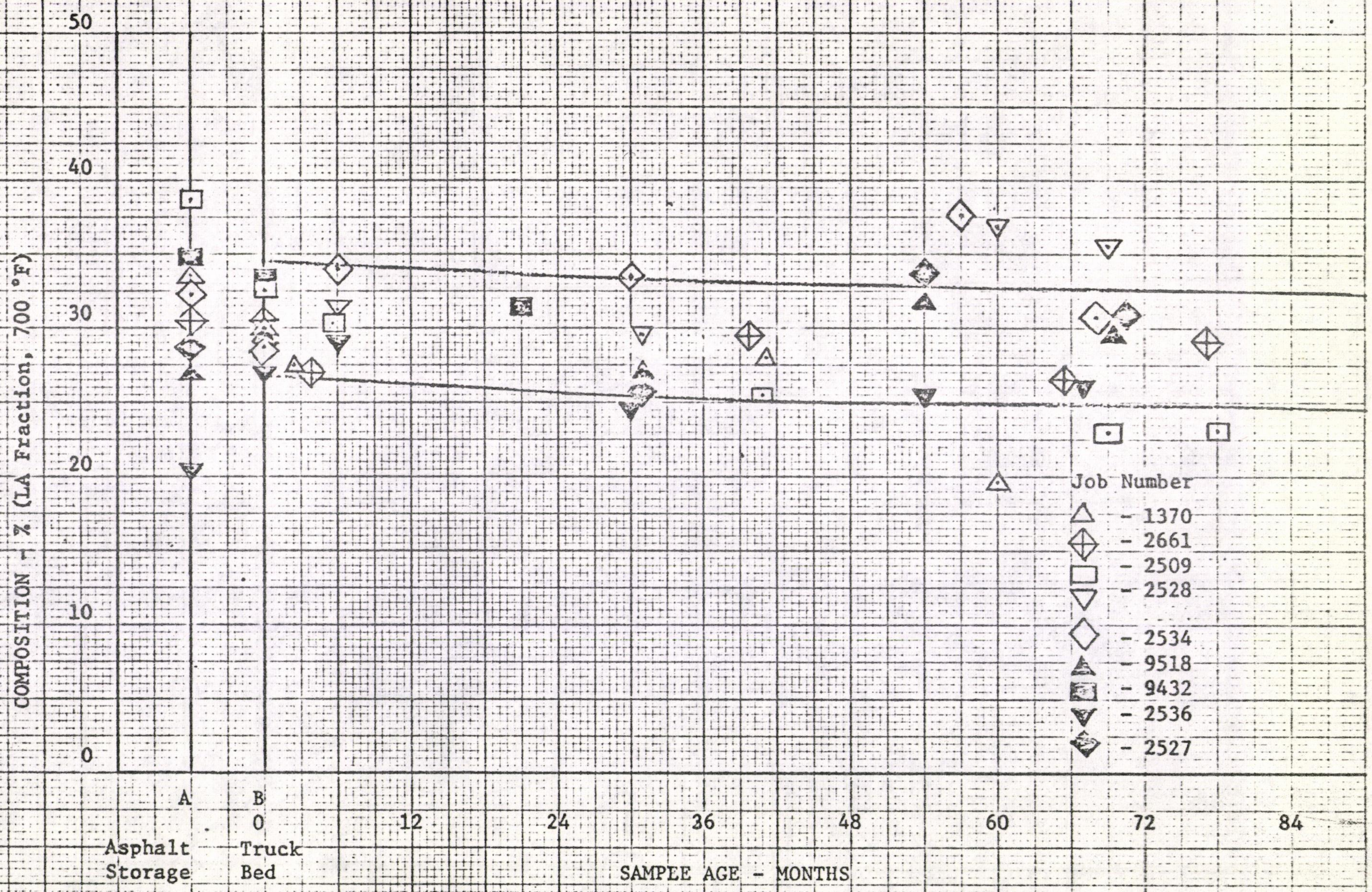

Figure 25. Composition as a function of Smaple Age (LA Fraction, 700 °F)

LA

Figure 26. Composition as a function of Sample Age (HA_1 Fraction, 700 °F)

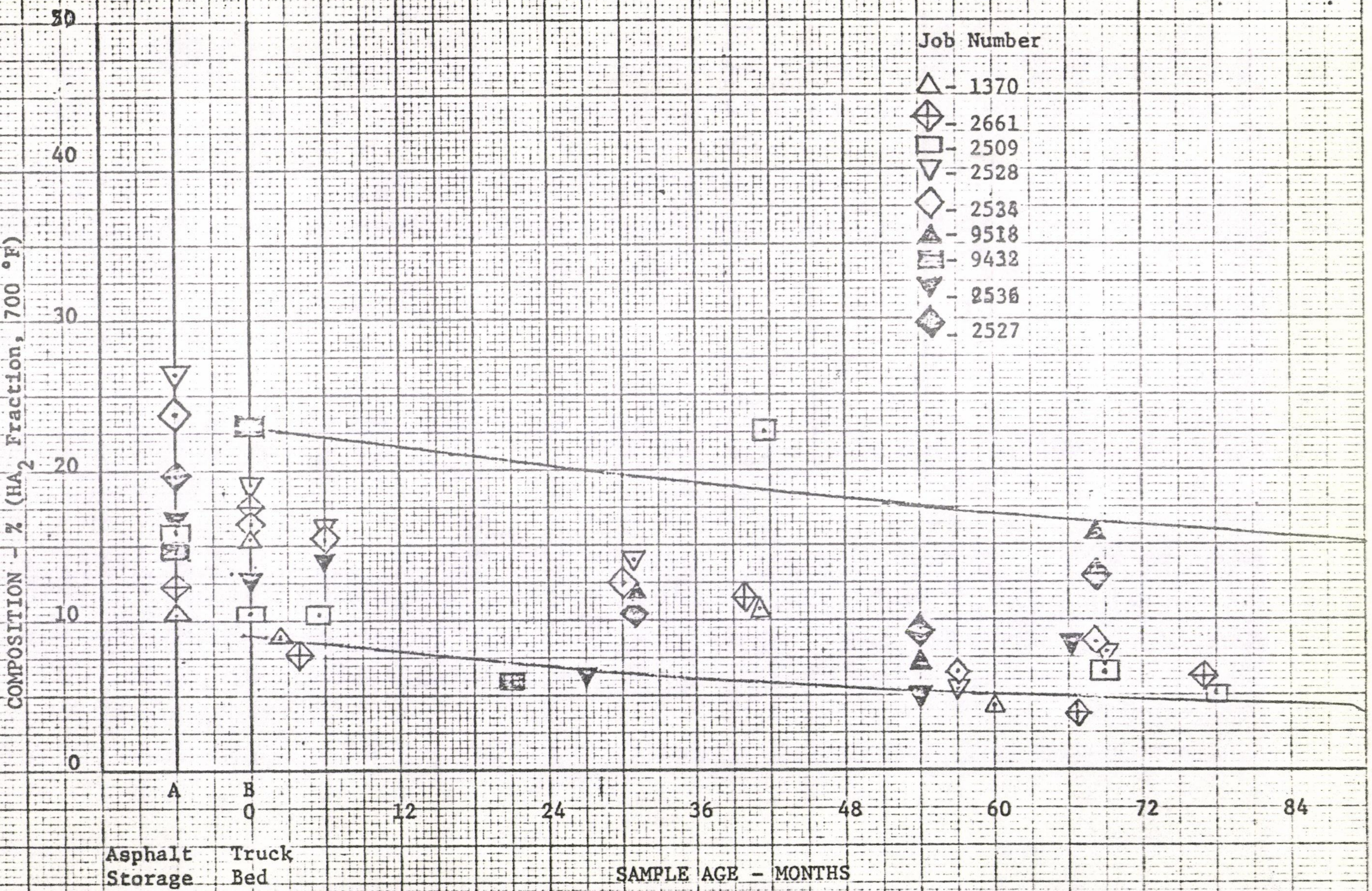

Figure 27. Composition as a function of Sample Age (HA_2 Fraction, 700 °F)

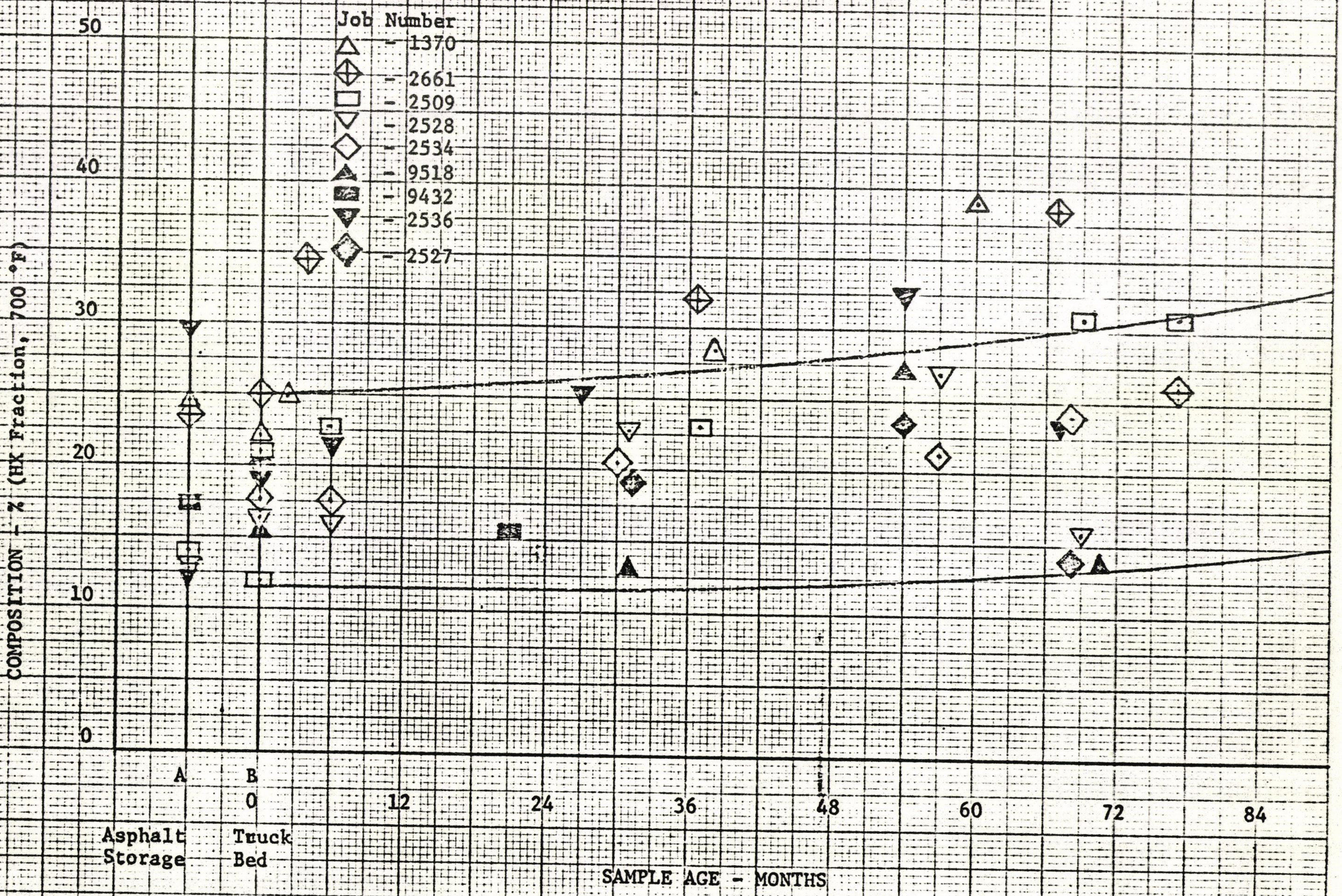

Figure 28. Composition as a function of Sample Age (HX Fraction, 700 °F)

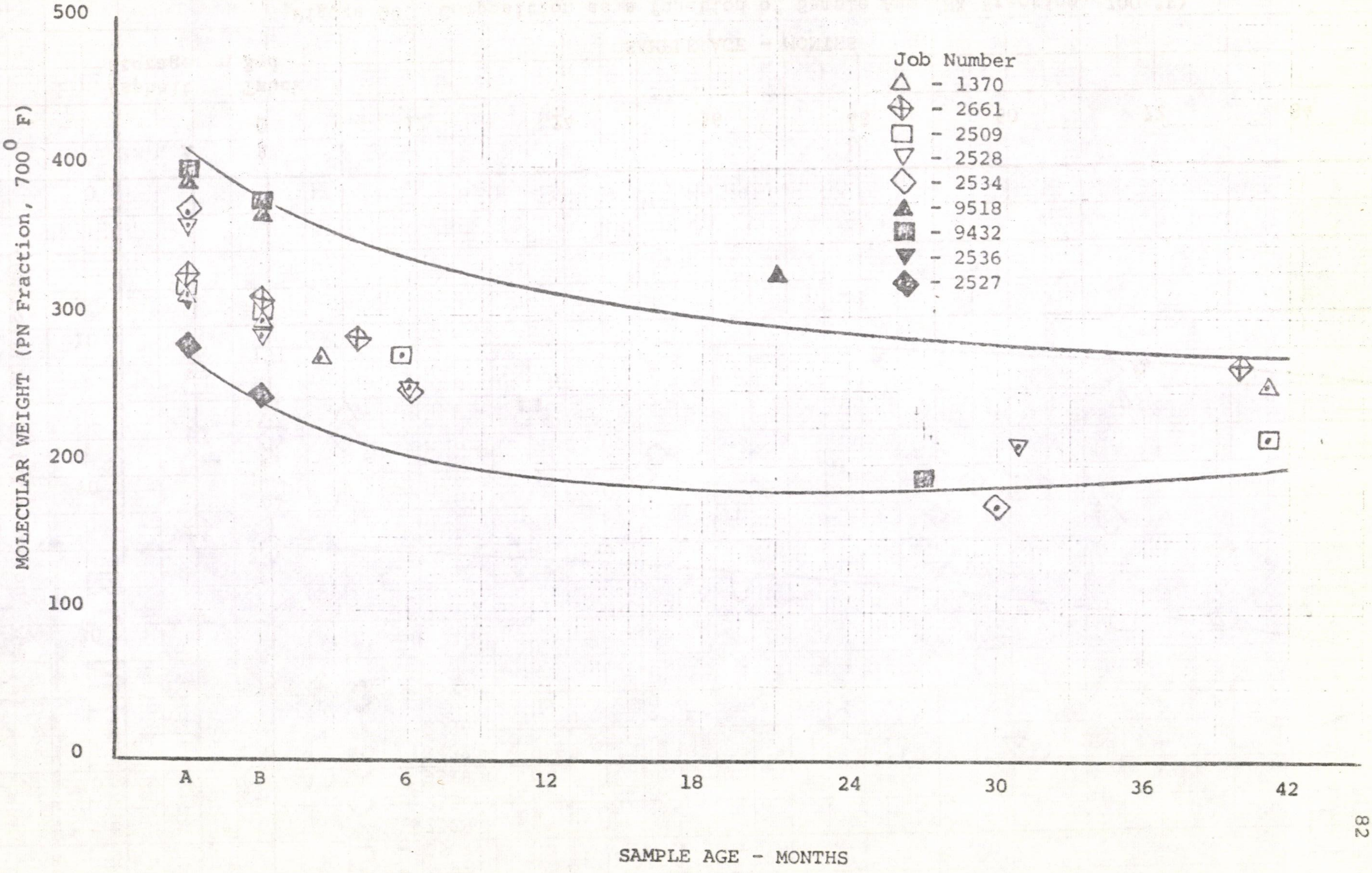

Figure 29. Molecular Weight as a function of Sample Age (PN Fraction, 700° F)

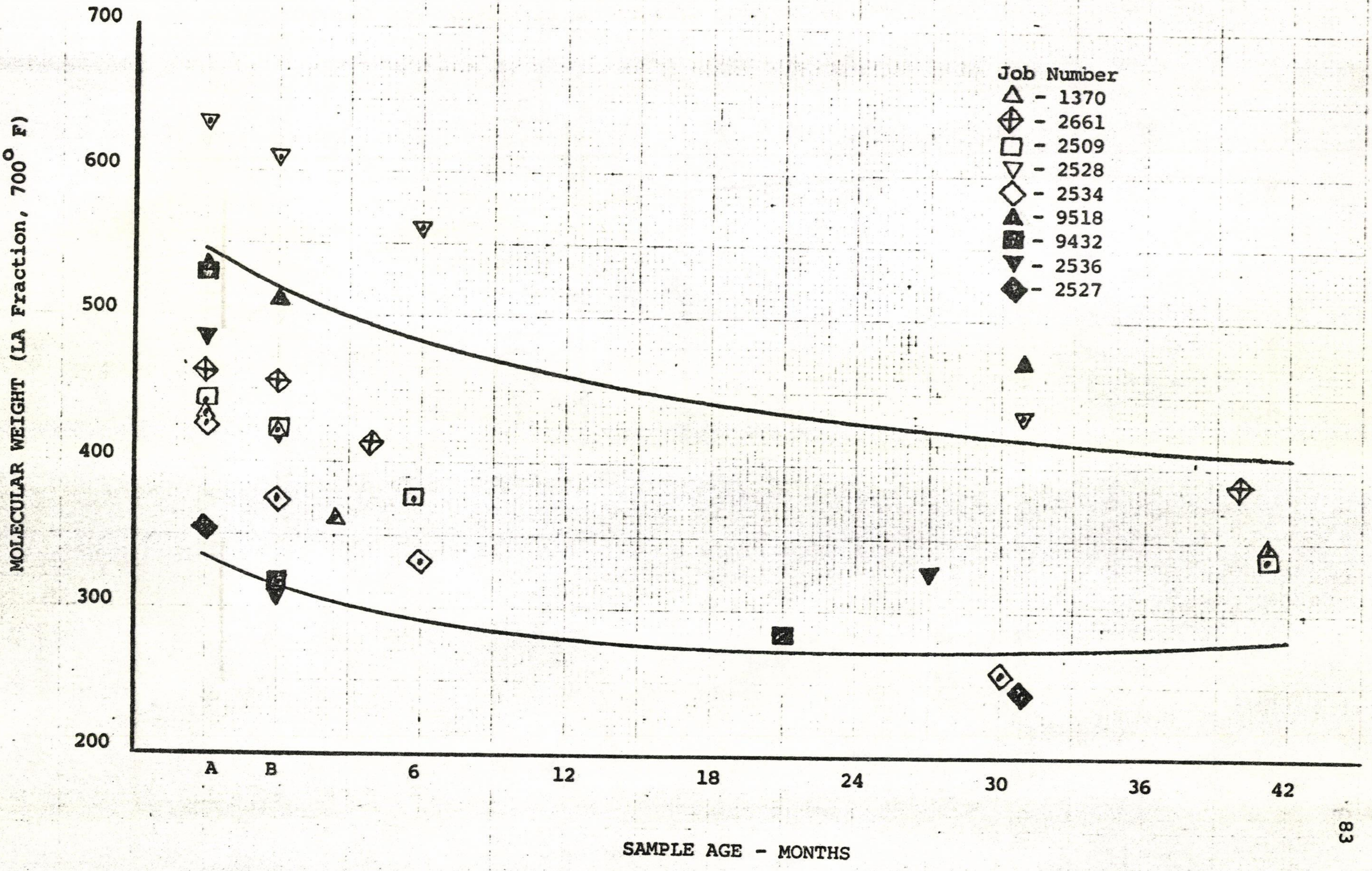

Figure 30. Molecular Weight as a function of Sample Age (LA Fraction, 700° F)

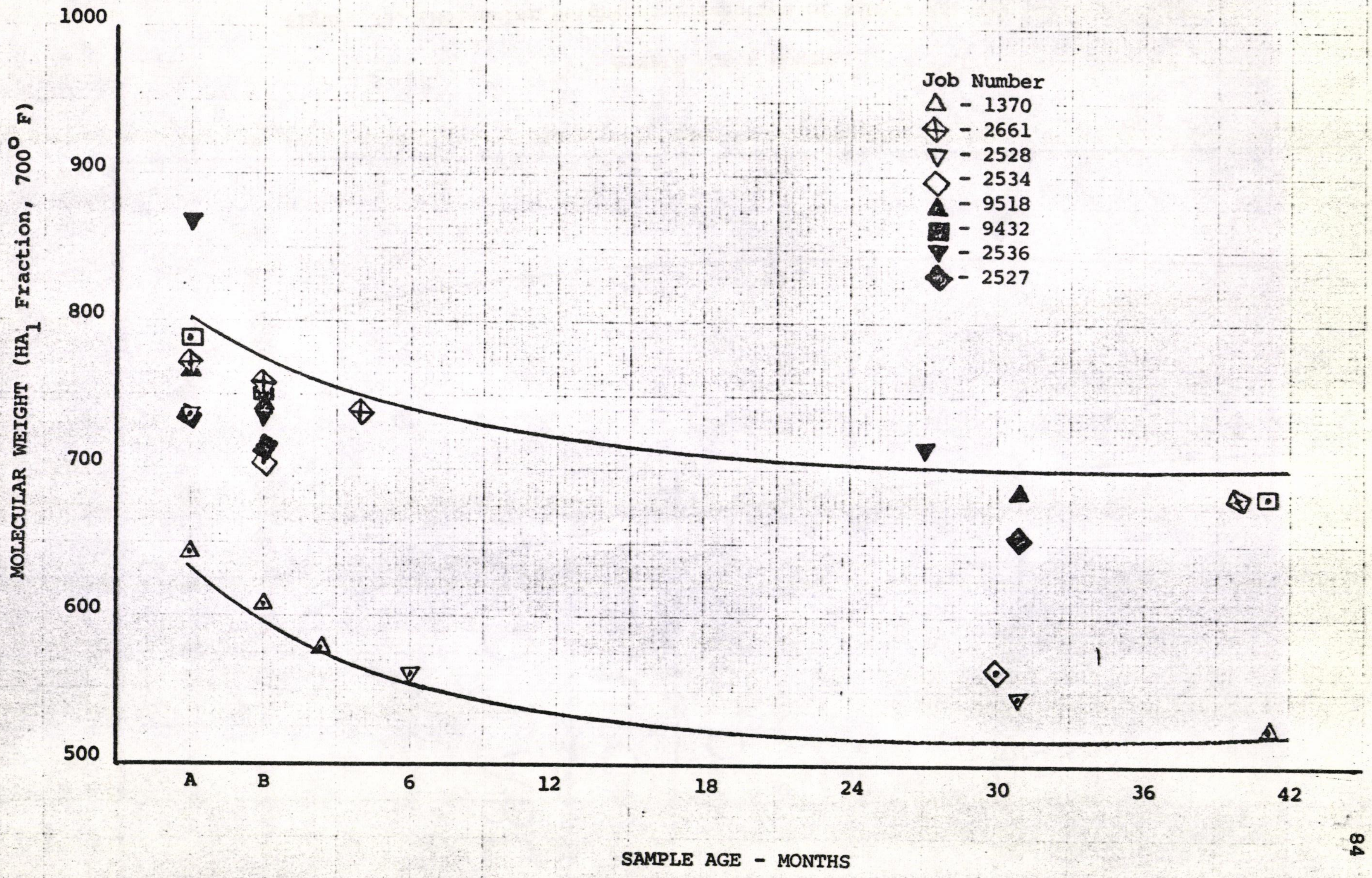

Figure 31. Molecular Weight as a function of Sample Age (HA_1 Fraction, 700° F)

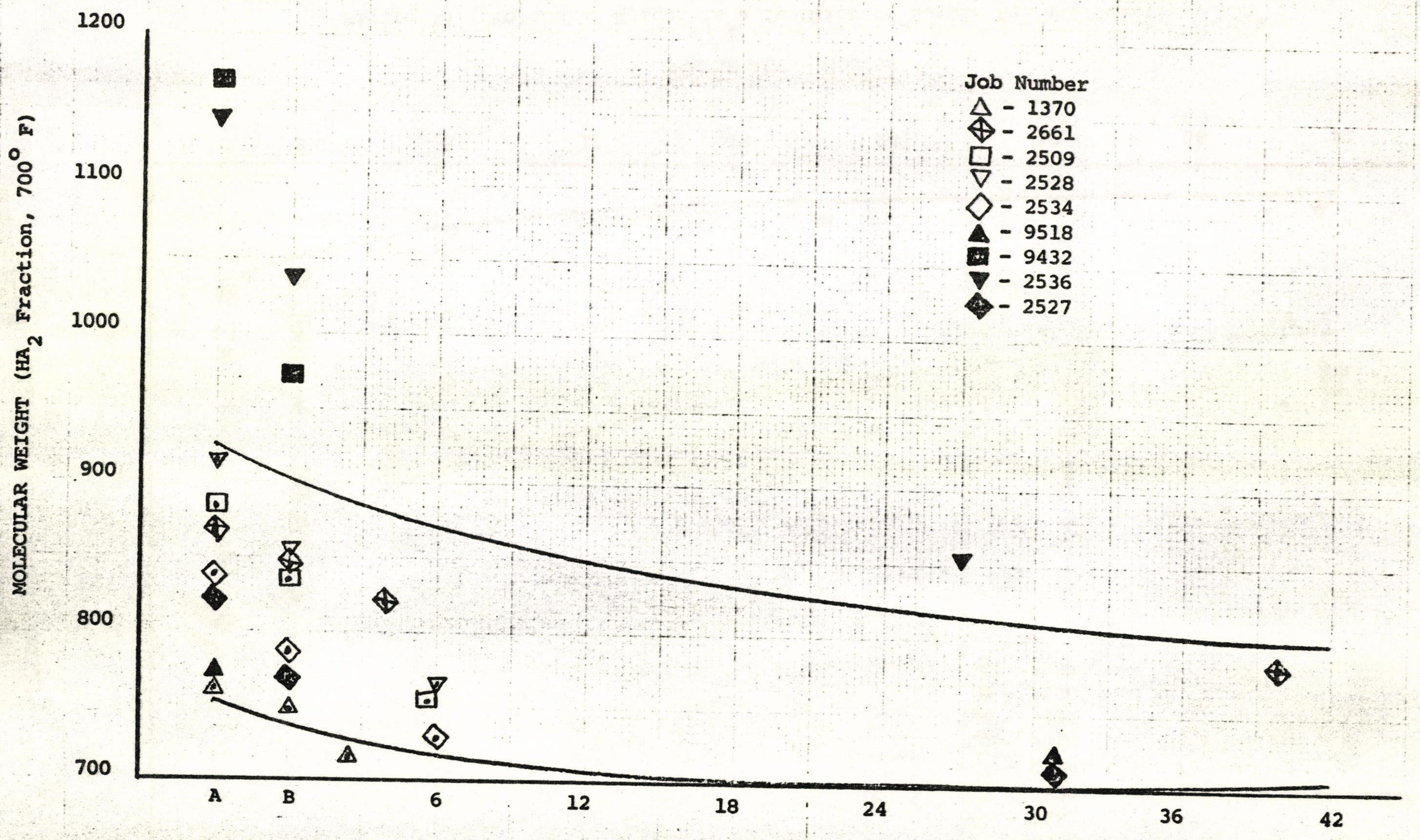

Figure 32. Molecular Weight as a function of Sample Age (HA_2 Fraction, 700° F)

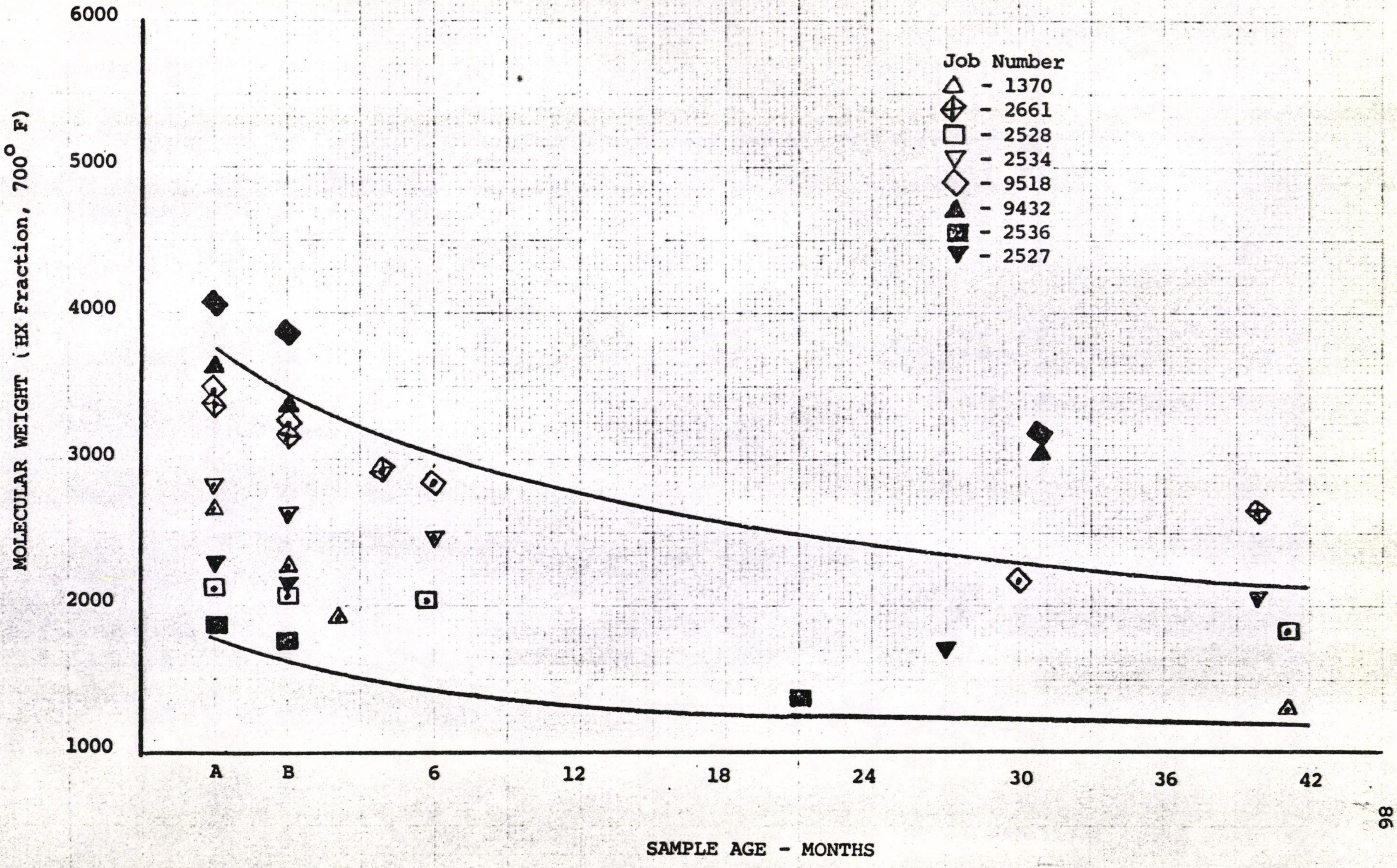

Figure 33. Molecular Weight as a function of Sample Age (HX Fraction, 700° F)

DISCUSSION OF RESULTS

The purpose of this investigation was to correlate physical properties with chemical composition of paving grade asphalts. Chemical composition and fraction molecular weight data were used as independent variables in a regression analysis to correlate these properties with stress relaxation moduli, absolute viscosity, penetration and ductility. Another aspect of this study was to note how the independent variables varied with sample age.

To indicate the magnitude of the correlation work, 206 separate linear equations were involved in the regression analysis. Of these, 114, or 55% yielded a multiple correlation coefficient (MCC) of 0.75 or better. This figure is considered good in most statistical correlation work.

There were 75 equations, or 36% of the total, with a MCC of 0.85 or better and 46 or 22% of the total, with a MCC of 0.90 or better. The 46 expressions are reported in Tables 1 through 6. It was decided that only those equations with a 0.90 MCC or better would be reported because of the large total number of equations, some of which had such low MCC's that they would have little value in predicting the dependent variable.

Regression analysis equations are only as good as the data used in arriving at the constants. Also, the data for the independent variables must be obtained using the procedures outlined in this report.

The authors are fully cognizant of the fact that more experimental data would be desirable to improve the regression analysis equations from the standpoint of MCC and standard error of estimate. For example, on page 63 E sample, 700 °F, 60/200 PEN, the regression equation is suspect. A rerun on existing data produced the same results.

Any of the 0.75 MCC or better equations would be adequate for predicting viscosity (μ) ductility (DUCT), or penetration (PEN) for the given sample parameters.

A generalized representation of G_r as a function of time is presented in Figure 10. The results indicate that the initial stress imparted to the asphalt samples drops off rapidly in a short period of time (approximately 100 seconds) and then relaxes much more slowly as a greater time interval elapses. It is not possible to relate this relaxation phenomenon to the chemical properties through regression analysis with the computer program as used. Since the stress relaxation is a time-dependent quantity, it could not be used as the dependent variable of a regression equation.

Figure 10 depicts the generalized shape of the stress relaxation curves. Detailed data have been presented in reports by Lamb (13) and Miller (15).

From Figures 11, 12, and 13, it can be seen that absolute viscosity increases with sample age while ductility and penetration decrease with sample age. These trends are to be expected since asphalt tends to oxidize and form more asphaltenes with age as shown for example, in Figures 18 and 28. Figures 11, 12, and 13, are generalized depictions of actual data presented in previous reports by Bissett (2) in HRC #17, a companion project to HRC #21.

Figures 14 through 33 depict the effect of aging upon the chemical group constituents and the molecular weight of the fractions. An envelope was drawn on each plot to indicate the upper and lower bounds of composition for each fraction. As the sample ages, there is an increase in asphaltenes content at the expense of the PN, LA and HA fractions which show a slow decline. The greatest composition change took place in the pug mill.

In the opinion of the authors, these changes probably occur due to the oxidation of the asphalt fractions since the elements for oxidation are present, namely heat, light, pressure, and the presence of atmospheric oxygen. Whether polymerization occurs or not could not be determined in this study. Perhaps research ought to be conducted on what mechanism(s) do take place.

Figures 24 through 28 include F and G samples which were taken approximately five and six years, respectively, after the pavements were originally laid.

Jones (12) indicated that he obtained a contamination of the PN fractions by low molecular weight aromatic compounds, LA, in his investigation. He made several suggestions such as precipitating the aromatics with 1-butanol or precipitating the saturated hydrocarbons with chilled acetone. These modifications were tried several times. Although the precipitation methods were satisfactory they were time-consuming. It was found that by activating the Porocel adsorbent at 700 °F rather than at 270 °F, essentially the same improvement in reproducibility could be achieved in the chromatographic separations.

It was found that activating the Porocel at 270 °F, the reproducibility or results varied on the average ± 7% based on the total compositional analysis. By activating the adsorbent at 700 °F, the reproducibility on all samples was improved to on the average ± 5.0% based on the total compositional analysis.

The scatter of data outside the envelopes could be attributed to where the sample was obtained, how the sample was extracted and subsequently handled in the chemical analysis. These are some of the variables which can occur in the procedures used.

Liquid chromatographic techniques generally produce less accurate results than precipitation methods, e.g. Rostler's method. However, the time saved in using a chromatographic method offsets the additional accuracy gained by long precipitation methods. In precipitation methods, losses do occur due to solubility of a fraction in the solvent.

If one wants greater accuracy then the associated cost in equipment and time would have to be accepted. However, it is a moot point at this period in time whether more accurate methods are warranted in the development of specification methods from chemical compositional analyses.

The molecular weights could be determined on the average with a reproducibility of ± 2.0%.

No visual inspections were reported concerning the condition of the pavements from which the various samples were obtained. Therefore, it was not possible to assess qualitatively the effects on composition on pavement durability.

CONCLUSIONS

The results of this study indicate that the regression analysis technique can be used to correlate the empirical physical properties of paving-grade asphalts with the chemical properties. The results also show that there is a definite influence on the physical properties of asphalt by the chemical properties and that these chemical properties change with age.

The most notable chemical change is that the asphaltene content increases with age while the other fractions decrease with age.

It is possible to take a sample of asphalt of a given age and predict the empirical physical properties based on a knowledge of the chemical properties. The equations developed with a multiple correlation coefficient of 75% or higher would give the most accurate results.

RECOMMENDATIONS

Based upon the conclusions of this study, it is recommended that:

1. Further regression work should be performed. A non-linear approach would probably fit more of the data and result in more equations with a more favorable multiple correlation coefficient.
2. The same non-linear approach could be used to fit the modulus of elasticity (G_r) data to an equation. Future work should be concerned with determining a relationship between G_r and the empirical physical properties.
3. More project samples should be obtained since the statistical evaluations would be more accurate due to the fact that the calculations are based on a larger number of samples.
4. All future chromatographic separations should be carried out on Porocel activated at 700°F, since this temperature seemed to give more consistent results.
5. Visual inspections of the pavement should be carried out to determine the effects of composition change with age on the pavement condition.
6. A modified Rostler-type parameter should be developed (18) on the basis of the chemical properties of this study. This parameter would be used to relate composition to durability of asphalt pavement.

7. The State Highway Department should continue to obtain core samples each year throughout the life of the pavement in order to determine the ultimate composition of the binder.
8. Since the greatest composition change took place in the pug mill, a study should be initiated to determine what occurs in this operation.
9. A long range study of what mechanism(s) occur(s) to cause the chemical composition change in the asphalt binder.

IMPLEMENTATION STATEMENT

Throughout this research project, any method proposed or developed was with the idea of ultimate implementation by State Highway Department laboratory personnel. Therefore, extremely sophisticated techniques and expensive equipment was avoided since both would be costly with regard to time, and the marginal gain in accuracy might not offset any accrued benefits.

The laboratory procedures presented in this report are such that a laboratory technician could perform the tests and present the results with a minimum amount of training.

The authors recommended that implementation of the chemical composition analyses be started as soon as possible at the conclusion of the major part of the project.

In the summer of 1970 the authors visited the State Highway Department Laboratory to instruct their personnel in the operation of the chemical analysis equipment. During that summer, a laboratory technician performed the chemical composition analysis on the F samples using the 700 $^{\circ}F$ technique. At the University laboratory the same analyses were conducted. Once a week, the results were checked and assistance was given by the University personnel when procedural questions arose. During the following summer an additional set of samples were analyzed and these data were plotted as the G samples.

1. It is further recommended that core samples be obtained each year from those highways still in service and that the data be plotted on the chemical composition graphs using

700 °F technique,

2. Highway Department personnel inspect the condition of the pavement when samples are taken to note any deterioration, especially as a result of binder failure, and
3. Highway personnel keep a log on each of the jobs in this project to record the performance of the pavement.

If the above implementation steps are incorporated, then a better understanding of the requirements for future pavement specifications may be obtained.

Since physical properties are very dependent upon the chemical composition of any material, it is absolutely essential to know within what ranges of composition the materials used give satisfactory service.

Before any specifications are modified, it is recommended that the chemical composition analyses be performed on every new asphalt highway. Old specifications should not be totally abandoned until more experience with the chemical composition analyses is obtained. Confidence in the new method will develop with experience.

In the long range, specifications may be developed limiting the ranges of chemical constituents which will produce a durable asphaltic binder. The tightening of asphalt specifications will result in a higher asphalt binder cost but the potential savings in highway maintenance and longevity should offset the initial cost.

LITERATURE CITED

1. "Asphalt Handbook, The," Manual Series Number 4, July 1962 Edition, The Asphalt Institute, College Park, Maryland, 40 (1963)

2. Bissett, J.R., "Changes in Physical Properties of Asphalt Cement Under Service Conditions," Highway Research Project 17 Final Report, Civil Engineering Dept., University of Arkansas, Fayetteville, Ark., pp. 4-8 (1964)

3. Buechley, T.C., "The Design and Construction of a Rotational Viscometer," M.S. Thesis, Chemical Engineering Dept., University of Arkansas, Fayetteville, Ark., 28 (1966)

4. "Concepts and Applications of Regression Analysis," IBM Applications Manual E20-0180, Data Processing Division, International Business Machines Corporation, White Plains, New York, pp. 1-8 (1966)

5. Corbett, L.W. and Swarbrick, R.E., "Composition Analysis Used to Explore Asphalt Hardening," Proceedings, Association of Asphalt Paving Technologists, 31 104 (1960)

6. Corbett, L.W. and Swarbrick, R.E., Proceedings, Association of Asphalt Paving Technologists 27, 107 (1958)

7. Corbett, L.W. and Swarbrick, R.E., Proceedings, Association of Asphalt Paving Technologists, 29, 104 (1960)

8. Draper, N.R. and Smith, H., "Applied Regression Analysis," John Wiley and Sons, Inc., New York, N.Y., pp. 33-118 (1966)

9. Glasstone, Samuel, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., 2nd Edition, pp. 637-750 (1951)

10. Gotolski, W.H., et al, "A Study of Physical Factors Affecting the Durability of Asphaltic Pavements," Research Report IR-8, Civil Engineering Department, Pennsylvania State University, University Park, Penn., pp. 17-20 (1967)

11. Hoiberg, A.J., "Bituminous Materials: Asphalts, Tars, and Pitches," Volumes I and II, Interscience Publishers, Inc., New York, N.Y., pp. 27-33 (1965)

12. Jones, R.N., "A Study of the Chemical Composition of Asphalts Used on Arkansas Roads," M.S. Thesis, Chemical Engineering Department, University of Arkansas, Fayetteville, Arkansas, pp. 13-25 (1967)

13. Lamb, C.W., "The Effect of Chemical Composition on the Rheological Properties of Asphalt," Ph.D. Dissertation, Chemical Engineering Department, University of Arkansas, Fayetteville, Arkansas, pp. 29-310 (1967)

14. Majors, A.B. and Couper, J.R., "A Chemical Composition Study of Asphalt," Report to the Arkansas State Highway Department, Chemical Engineering Department, University of Arkansas, Fayetteville, Arkansas pp. 12-24 (1969)

15. Miller, C.H., "Changes in Elasticity of Paving Grade Asphalts During Processing and Road Service," M.S. Thesis, Chemical Engineering Department, University of Arkansas, Fayetteville, Arkansas,pp. 13-63 (1968)

16. Miller, Irwin, and Freund, J.E., "Probability and Statistics for Engineers," Prentice-Hall, Inc., Englewood Cliffs, New Jersey 140 (1965)

17. Rostler, F.S. and White, R.M., "Composition and Changes in Composition of Highway Asphalts 85-100 Penetration Grade," Proceedings, Association of Asphalt Paving Technologists, <u>31</u> 35 (1962)

18. Spiegel, Murray R., "Theory and Problems of Statistics," Schaum's Outline Series, McGraw-Hill Book Company, New York, N.Y., pp. 69-219 (1961)

19. Stanton, R.G., "Numerical Methods for Science and Engineering," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, pp. 52-55 (1961)

20. Traxler, R.N., "Asphalt, Its Composition, Properties and Uses," Reinhold Publishing Corp., New York, N.Y. (1961)

21. Traxler, R.N., "Correlation of Composition with Durability and Rheology of Asphalts," Proceedings, American Society for Testing and Materials, <u>63</u>, 1235 (1963)

22. Tucker, J.R., and Schweyer, H.E., Industrial Engineering Chemistry, <u>4</u> 51 (1965)

23. "Ultracentrifugal Theory," Model E Ultracentrifuge Instruction Manual, SPINCO Division, Beckman Instruments Incorporated, Palo Alto, California,pp. 5-18 (1968)

24. Van Wazer, J.R., Lyons, J.W., Kim, K.Y., and Colwell, R.E., "Viscosity and Flow Measurement," Interscience Publishers, Inc., New York, N.Y., 49 (1963)

APPENDICES

APPENDIX I

SAMPLE CALCULATIONS

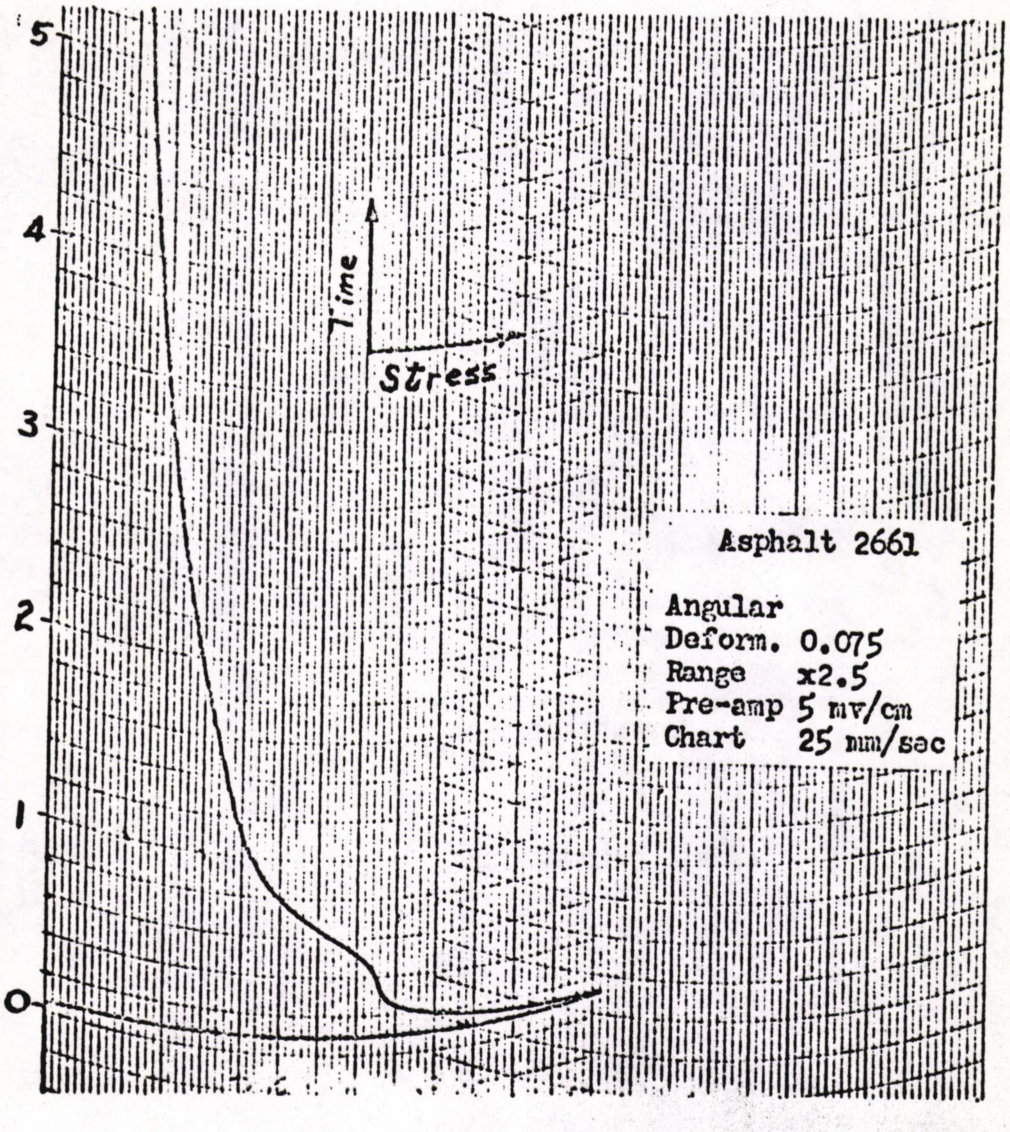

Figure 9. Recorder Chart for Stress Relaxation

Stress-Relaxation Modulus:

A typical experimental stress-relaxation curve is shown in Figure 9 for Asphalt 2661. The magnitude of the stress-relaxation modulus for this asphalt sample is calculated by the same method as used by Lamb (14) and Miller (16):

The conicylindrical viscometer had the following dimensions:

$a = 1.270$ cm

$b = 1.905$ cm

$h_1 = 1.588$ cm

From Equation (1):

$$r_m = \left[\frac{2a^2b^2}{a^2+b^2}\right]^{\frac{1}{2}}$$

$$r_m = \left[\frac{2(1.270)^2(1.905)^2}{(1.270)^2+(1.905)^2}\right]^{\frac{1}{2}}$$

$$= 1.494 \text{ cm}$$

and

$$f = \frac{(1.905)^2 - (1.270)^2}{(1.905)^2 + (1.279)^2}$$

$$= 0.3846$$

By trial-and-error from Equation (2)

$$\delta = 0.3704 \text{ radians } (21.22^{\circ})$$

From Equation (3)

$$\theta = \pi/2 - \delta$$

$$\theta = \pi/2 - 0.3704$$

$$= 1.2004 \text{ radians } (68.78^\circ)$$

Therefore $h_o = 1.588 + 2 \left[(1.270) \cot (68.78^\circ) - (1.494) \cot (79.39^\circ)\right]$

$$h_o = 2.014 \text{ cm}$$

Substituting the above quantities into Equation (6)

$$G_r(t) = \frac{T'(t)/2.6\ \gamma}{2\pi\ (1.494)^2\ (2.014)\ \left[1 + 2\ (1.494)/3\ (2.014)\ \cos\ (10.61^\circ)\right]}$$

$$= (9.046 \times 10^{-4} \text{ cm}^{-3}) \frac{T'(t)}{\gamma}$$

Using the reaction torque sensor calibration of 20 in-0z/mv and noting from Figure (9) that after two seconds, the chart reading is 1.97 cm:

$$T'(2) = (1.97 \text{ cm})\ (5\text{mv/cm})\ (2.5 \times 20 \text{ in-oz/mv})\ (2.5 \text{ cm/in}) \times (\text{lb}/16 \text{ oz})\ (4.448 \times 10^5 \text{ dynes/lb})$$

$$= 3.48 \times 10^7 \text{ dyne - cm}$$

Finally $G_r(2) = (9.046 \times 10^{-4} \text{ cm}^{-3}) \dfrac{(3.48 \times 10^7 \text{ dyne - cm})}{0.075 \text{ radians}}$

$$G_r\ (2) = 4.19 \times 10^{16} \text{ dynes / cm}^2$$

A computer program for calculating G_r is presented in Appendix III.

Molecular Weight Determination:

Benzil (1) weight: 0.0617 grams, w_2

Camphor weight: 0.9920 grams, w_1

Solution Freezing Point: 317°F

Pure Camphor Freezing Point: 337°F

K_f: 67.85

$\Delta T_f = 20^{\circ}F$

From Equation (9): $$M_2 = K_f \frac{1000\ w_2}{\Delta T_f w_1}$$

$$M_2 = (67.85)\ \frac{(1000)\ (0.0617)}{(20)\ (0.9920)}$$

$$M_2 = 211.00$$

A computer program for calculating molecular weights is presented in Appendix III.

APPENDIX II

NOMENCLATURE

NOMENCLATURE

Symbol	Definition
a	radius of stator of conicylindrical viscometer annulus (cm)
A_1	first acidaffins fraction
A_2	second acidaffins fraction
b	radius of rotor of conicylindrical viscometer annulus (cm)
c	concentration (grams/cm^3)
DUCT	ductility (cm)
F'	mean stress (dynes/cm^2)
F	Goodness of Fit
G_r	stress relaxation modulus (dynes/cm^2)
h_o	effective stator length (cm)
h_1	length of inner cylinder of viscometer (cm)
HA_1	first heavy aromatic fraction
HA_2	second heavy aromatic fraction
HMA	heavy molecular weight multi-ring compounds
H_s	saturated hydrocarbon fraction
HX	asphaltene fraction
K_e	boiling point elevation constant
K_f	freezing point depression constant
LA	light aromatic fraction
LMA	low molecular weight multi-ring compounds
MCC	multiple correlation coefficient, R^2
$\bar{M}_n$	number average molecular weight
M_2	molecular weight

M_w	weight average molecular weight
N	nitrogen base fraction
n_i	number of molecules of molecular weight M_i
PEN	penetration (tenths of millimeter)
PN	paraffin-naphthene fraction
R	gas constant (8.313 x 10^7 ergs/degrees mole)
r_m	mean radius of conicylindrical viscometer annulus (cm)
S	standard error of estimate
s	standard deviation
$s(\alpha,\beta)$	least squares summation
SH	Arkansas State Highway
T	absolute temperature (^{o}K)
t	time (sec)
T_e	temperature elevation (^{o}F)
T_f	temperature depression (^{o}F)
US	United States Highway
$\bar{v}$	partial specific volume (cm^3/gram)
w_1	weight of solvent (grams)
w_2	weight of solute (grams)
x	distance from axis of rotation (cm)

GREEK

δ	angular separation of cones
ε_o	sample strain (radians)
γ	angular displacement of rotor (radians)
ρ	density (grams/cm^3)

ρ_{xy}	simple correlation coefficient
θ	half angle of stator cone of conicylindrical viscometer (radians)
μ	viscosity (Poises)
ω	angular velocity (radians/sec)

COMPUTER NOMENCLATURE

Bissett's Viscosity = f (composition) A samples 270F

This is J.R. Bissett's (7) absolute viscosity for the A samples used as the dependent variable in the regression equation versus the compositions of the A samples which were separated on Porocel activated at 270°F and used as the independent variables.

Bissett's Viscosity = f(mol.wt.) A samples 300F

This is J.R. Bissett's absolute viscosity used as above with the exception that the independent variables are now the molecular weights of the asphalt fractions used above, Porocel activated at 300°F.

Ductility = f (composition) A 270 45/1

This is J.R. Bissett's ductility as dependent variable with compositions as independent variables for A samples, Porocel activated at 270°F, ductility measurements carried out at 45°F and 1.0 cm/sec.

Ductility = f(mol.wt.) A 300 77/5

This is J.R. Bissett's ductility as above with the exception that the independent variables are now the molecular weights of the asphalt fractions used above, Porocel activated at 300°F, ductility measurements carried out at 77°F and 5.0 cm/sec.

Penetration = f (composition) A 270 77/100

This is J.R. Bissett's penetration as dependent variable with compositions as independent variables for A samples, Porocel activated at 270°F, and penetration measurements carried out at 77°F with a 100 gram weight.

Penetration = f (mol.wt.) A 300 77/200

This is J.R. Bissett's penetration as above with the exception that the independent variables are now the molecular weights of the asphalt fractions used above. Porocel activated at 300°F, a 200 gram weight.

Regression Equation Format:

$$y = a + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5$$

a = constant term, final step

b_1 = VAR 1, coefficient of x_1 x_1 = PN (composition or molecular weight)

b_2 = VAR 2, coefficient of x_2 x_2 = LA (composition or molecular weight)

b_3 = VAR 3, coefficient of x_3 x_3 = HA_1 (composition or molecular weight)

b_4 = VAR 4, coefficient of x_4 x_4 = HA_2 (composition or molecular weight)

b_5 = VAR 5, coefficient of x_5 x_5 = HX (composition or molecular weight)

Example:

Ductility = F (composition) A 700 60/5

$$\text{Duct} = 104.955010 - 0.89945987\text{PN} - 1.65165913\text{LA} + 0.31511427\text{HA}_1 + 0.80946998\text{HA}_2 - 1.14568651\text{HX}$$

APPENDIX III

COMPUTER PROGRAMS

COMPUTER PROGRAMS

The program used to calculate G_r as a function of time from the recorder chart readings is as follows:

```
     DIMENSION RANGE (600), CM (600), T (600), GR (600), S (14), N (14)
     READ (5,5) (s(J), J = 1, 14)
     READ (5,6) (N(J), J=1, 14)
     Cl = 20.*254/16.*4.448*1.**5*5.
952  DO 22J = 1, 14
     M = N(J) + M
     M = 0
 22  CONTINUE
     READ (5,5) (RANGE (J), CM(J), J = 1, M)
     KL = 0
     L = 1
200  DO 34 I = 1, M
     IF (I.EQ.L) GO TO 160
     GO TO 14
160  WRITE (6,99)
     KL = KL + 1
     C4 = 0.00914/S(KL)
     L = N(KL) + L
 14  T (I) + Cl*RANGE (I) * CM (I)
     GR (I) = C4 * T (I)
     WRITE (6,18) RANGE (I), CM (I), T (I), GR (I)
 34  CONTINUE
```

```
  99 FORMAT (/ / / /)
  18 FORMAT (1X, F10.2, 5X, F10.2, 5X, F15.0, 5X, F15.0/)
   5 FORMAT (8F10.3)
   6 FORMAT (8I10)
1234 STOP
     END
```

The input data are stress, S(J), and time, N(J), and printout is the range of the recorder, Range (I), the distance along the time axis, CM (I), torque, T (I) and G_r, GR(I). Each set of these numbers is printed according to the elapsed time of the stress relaxation, allowing G_r to be plotted as a function of time (Figure 10).

It was not possible to obtain a copy of the computer program used for the multiple stepwise regression analysis. This situation was due to the fact that the program was purchased from IBM on tape with instructions for entering and transforming data. It was not possible to instruct the computer to print out the program. However, the program embraced the concepts presented in the Theoretical Discussion, (pp. 21-27)

Typical results from the computer print out of one regression analysis of viscosity as a function of the molecular weights of the fractions for E samples which were separated on Porocel activated at 700°F follow.

```
              VISCOSITY = F( MOL. WT.) E SAMPLES 700 F

STANDARD DEVIATIONS

VAR (1) =  54.151 VAR (2) =  77.371 VAR (3) =  85.461 VAR (4) = 68.201

VAR (5) = 685.481 VAR (6) = 12219.86

SIMPLE CORRELATION COEFFICIENTS

VARS (1,1) = 1.00 VARS (1,2) = 0.381 VARS(1,3) = -0.324 VARS(1,4) = -0.219

VARS (1,5) =-0.267VARS (1,6) = 0.039

VARS (2,2) = 1.000VARS (2,3) = 0.229 VARS(2,4) = 0.210  VARS(2,5) =  0.183

VARS (2,6) = -0.116

VARS (3,3) = 1.000VARS (3,4) = 0.793 VARS(3,5) = 0.555  VARS(3,6) =  0.22

VARS (4,4) = 1.000VARS (4,5) = 0.240 VARS(4,6) = 0.384

VARS (5,5) = 1.000VARS (5,6) = -0.462

STEP NUMBER 1    .     ENTER VARIABLE 5

STANDARD ERROR OF ESTIMATE = 11587.221

MULTIPLE CORRELATION COEFFICIENT = 0.462

GOODNESS OF FIT, F( 1, 7) = 1.897

CONSTANT TERM = ************

 VAR              COEFF               STD DEV COEFF

  5              -8.232                5.976

STEP NUMBER 2          ENTER VARIABLE 3

STANDARD ERROR OF ESTIMATE = 9426.234

MULTIPLE CORRELATION COEFFICIENT = 0.744

GOODNESS OF FIT, F ( 2, 6) = 3.722

CONSTANT TERM = 3305.927490
```

```
 VAR                 COEFF              STD DEV COEFF

  3                100.296               32.436

  5                -15.172                5.844

STEP NUMBER 3            ENTER VARIABLE 2

STANDARD ERROR OF ESTIMATE = 10144.478

MULTIPLE CORRELATION COEFFICIENT = 0.754

GOODNESS OF FIT, F ( 3, 5) = 2.202

CONSTANT TERM = 7806.076

 VAR                 COEFF              STD DEV COEFF

  2                -20.278               45.020

  3                103.675               35.802

  5                -14.988                6.305

STEP NUMBER 4            ENTER VARIABLE 1

STANDARD ERROR OF ESTIMATE = 11147.645

MULTIPLE CORRELATION COEFFICIENT = 0.764

GOODNESS OF FIT F ( 4, 4) = 1.403233

CONSTANT TERM = -1488.722

 VAR              COEFF                 STD DEV COEFF

  1               33.661                 59.022

  2              -31.820                 57.361

  3              111.024                 42.240

  5              -14.548                  7.027
```

```
STEP NUMBER 5         ENTER VARIABLE 4

STANDARD ERROR OF ESTIMATE = 12799.445

MULTIPLE CORRELATION COEFFICIENT = 0.767

GOODNESS OF FIT, F( 5, 3) = 0.858

CONSTANT TERM = -8133.536

 VAR          COEFF              STD DEV COEFF

  1           34.016               67.795

  2          -32.853               66.094

  3           94.473              101.867

  4           22.034               36.952

  5          -13.899                8.798


OBS    ACTUAL        ESTIMATE       RESIDUAL       ERROR

 1    45115.00      34975.02       10139.98        22.48

 2    35388.00      33128.65        2259.35         6.38

 3    44129.00      42358.74        1770.26         4.01

 4    24968.00      22905.41        2062.59         8.26

 5    11969.00      26618.45      -14649.45      -122.39

 6    18130.00      24262.87       -6132.87       -33.83

 7    31806.00      34532.13       -2726.13        -8.57

 8    46871.00      49942.67       -3071.67        -6.55

 9    33016.00      22668.04       10347.96        31.34

END-OF-DATA ENCOUNTERED ON SYSTEM INPUT FILE.
```

MOLECULAR WEIGHT PROGRAM

```
      DIMENSION WTASP (100), WTCAM (100), TMELT (100)
      WRITE 42, MWT (100), AMWT (100)
      READ 4,N
      READ 5, (WTASP (I), WTCAM (I), TMELT (I), I = 1,N)
C     WTASP IS THE WEIGHT OF ASPHALT IN GRAMS
C     WTCAM IS THE WEIGHT OF CAMPHOR IN GRAMS
C     TMELT IS THE MELTING TEMPERATURE OF SAMPLE
C     MWT IS MOLECULAR WEIGHT
C     AMWT IS AVERAGE MOL WT OF SAMPLES
      CONST + 67.85
C     CONST IS FREEZING POINT DEPRESSION CONSTANT
      TREF = 353.1
C     TREF IS THE MELTING POINT OF PURE CAMPHOR
   11 DO 14 I = 1,N
      DELTAT = TREF - TMELT (I)
      MWT (I) = CONST * (WTASP (I)/WTCAM (I))*(1.0 DELTAT)
   14 CONTINUE
      K = 1.
   17 CONTINUE
      M = K + 1.
      AMWT (K) = (MWT (K) + MWT (M))/2.
      WRITE 40, AMWT
      IF (K. GT. N) GO TO 54
```

```
      GO TO 17
   54 STOP
      END
```

The input data are the sample weight of asphalt fraction, weight of camphor, and melting temperature of mixture. The results printed out are the individual sample molecular weights and average molecular weight for the trial.