Cairo University/Massachusetts Institute of Technology Technological Planning Program

Performance of Paraffinic-Waxy Asphalt Cements In Egyptian Road Construction

Volume II Chemical and Physical Properties of Western Desert Asphalt Cements

Research Supervised By
A. Osman
and
Mohsen Baligh

Prepared By
Technology Adaptation Program
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Sponsored By
United States Agency for
International Development

TAP Report 80-5 June 1980

/1

EG-AAC-007
2630061
PN RRV-867
ISN 247157

PERFORMANCE OF PARAFFINIC-WAXY ASPHALT CEMENTS IN EGYPTIAN ROAD CONSTRUCTION

VOLUME II

CHEMICAL AND PHYSICAL PROPERTIES OF WESTERN DESERT ASPHALT CEMENTS

TAP Report 80-5

June 1980

263-0061-C-00-1001-00

PREFACE

This report is one of a series of publications which describe various studies undertaken under the sponsorship of the Technology Adaptation Program at the Massachusetts Institute of Technology.

The United States Department of State, through the Agency for International Development, awarded the Massachusetts Institute of Technology a contract to provide support at M.I.T. for the development, in conjunction with institutions in selected developing countries, of capabilities useful in the adaptation of technologies and problem-solving techniques to the needs of those countries. This particular study describes research conducted in conjunction with Cairo University, Cairo, Egypt.

In the process of making this TAP supported study some insight has been gained into how appropriate technologies can be identified and adapted to the needs of developing countries per se, and it is expected that the recommendations developed will serve as a guide to other developing countries for the solution of similar problems which may be encountered there.

Fred Moavenzadeh

Program Director

FOREWORD

A four-year research program entitled, "Performance of Paraffinic-Waxy Asphalt Cements in Egyptian Road Construction," sponsored jointed by the United States Agency for International Development and a group of Egyptian road construction companies was initiated in June 1979 by the Massachusetts Institute of Technology, MIT, and Cairo University, CU. The final objective of the project is to improve the performance of pavements constructed with the Egyptian paraffinic-waxy asphalts.

The first year research is principally aimed at achieving a better understanding of the important factors affecting the use of Egyptian asphalts in road construction. In particular, the work includes:

1. An intensive literature survey to benefit from the experience of others dealing with temperature-sensitive asphalts, and help in establishing preliminary quality control criteria for Egyptian waxy asphalts in pavement construction.

2. A careful planning of sampling, laboratory, and preliminary field evaluation programs to determine the properties of Egyptian asphalts. This includes the selection of representative roadway sections and the assimilation of pavement history and distress evaluation data.

3. An evaluation of the physical and chemical characteristics of Egyptian asphalt cements.

4. An evaluation of the properties of available Egyptain aggregates.

This report presents the results of an intensive experimental study to establish the fundamental properties of Egyptian asphalt cements produced from the Western Desert crude oils.

The research is supervised by Professors A. Osman, CU, and M. Baligh, MIT. The following individuals, listed alphabetically, have participated in the preparation of this report: A. Azzouz (MIT); F. Ezzat (Egyptian Petroleum Research Institute); A. Gadallah (CU); M. Noureldin (CU); L. Radwan (CU); E. Sarhan (Ain Shams University); A.S. Soliman, (CU); and M. Talaat (Road Research Laboratory).

ACKNOWLEDGEMENTS

The following individuals and/or organizations provided valuable contributions to this study:

Ministry of Transportation, The General Authority of Roads and Bridges

Eng. Ahmed Shawky
Chairman, The General Authority of Highways

Eng. Said El-Beih
Assistant Director, Road Research Laboratory

National Academy of Science, Egyptian Petroleum Research Institute

Dr. Fathy Ebaid
Chairman, Egyptian Petroleum Research Institute

Dr. Mohamed Rushdy
Director, Research Laboratories

Dr. Gaber El-Fayoomy
Research Staff Member

Ministry of Industry, El-Nasr Petroleum Company, Alexandria

Eng. Said Kandil
Chairman

Matching funds were provided by the following Egyptian road construction companies:

1. The Arab contractors (Osman Ahmed Osman & Co.):
   Eng. Hussein Osman

2. The Nile Company for Roads and Bridges:
   Eng. Ahmed El-Okaily

3. El-Nasr Contracting Company (Hassan Allam):
   Mr. Mohamed Fahmy Allam

4. The General Authority for Roads and Bridges:
   Eng. Ahmed Shawky

5. The Nile Company for Road Construction:
   Eng. Ahmed Moussa

6. The Nile Company for Desert Roads
   Eng. Tharwat Sakr

TABLE OF CONTENTS

	Page
Title Page	1
PREFACE	2
FOREWORD	3
ACKNOWLEDGEMENTS	5
TABLE OF CONTENTS	7
LIST OF TABLES	9
LIST OF FIGURES	10
CHAPTER 1. INTRODUCTION	11
CHAPTER 2. SAMPLING PLAN AND EXPERIMENTAL DESIGN OF THE STUDY	14
2.1 Sampling Plan	14
2.1.1 Refinery Asphalt Cement Samples	14
2.1.2 Contractor Asphalt Cement Samples	14
2.2 Design of Experiments	15
2.2.1 Refinery Samples	15
2.2.2 Contractor Samples	16
2.2.3 Comparison Between Refinery and Contractor Samples	17
2.3 Testing Procedures	18
CHAPTER 3. TEST RESULTS	20
3.1 Crude Oil Properties	20
3.2 Asphalt Cement Properties	21
3.2.1 Refinery Asphalt Cement Samples	21
3.2.2 Contractor Asphalt Cement Samples	24

CHAPTER 4. ANALYSIS OF RESULTS 40

4.1 Contractor Asphalt Cement Samples 40

4.2 Comparison Between the Refinery and Contractor Asphalt Cement Samples 41

CHAPTER 5. SUMMARY AND CONCLUSIONS 48

REFERENCES 52

APPENDIX A. TYPICAL CHARTS: CHEMICAL ANALYSIS 53

LIST OF TABLES

Table		Page
2.1	Asphalt Cement Tests and Their Procedures	19
3.1	General Physical and Chemical Characteristics of Some Western Desert Crude Oils	26
3.2	Chemical and Physical Characteristics of Western Desert Crude Oil Mixtures (Alexandria Refinery, Aug.-Oct., 1979)	27
3.3	Component Analysis of Western Desert Crude Oils	28
3.4	Component Analysis of Refinery Samples	29
3.5	Per Cent Proton Types Distribution in Some AC Refinery Samples	30
3.6	Per Cent Proton Types Distribution in Two Resin Samples	30
3.7	Per Cent Proton Types Distribution - NMR Spectroscopy of Wax	31
3.8	Physical Characteristics of Refinery Asphalt Cement Samples	32
3.9	Existing and Proposed Standard Specifications for the 60/70 pen Asphalt Cement	33
3.10	Component Analysis of Contractor AC Samples	34
3.11	Physical Characteristics of Contractor AC Surface Samples	35
3.12	Physical Characteristics of Contractor AC Middle Samples	36
4.1	Typical ANOVA Table (Kinematic Viscosity, Before TFOT)	44
4.2	Summary of ANOVA; Contractor Samples	45
4.3	Summary of Physical and Chemical Properties of Refinery and Contractor Samples	46
4.4	Test of Difference Between Means for Refinery and Contractor Samples	47

LIST OF FIGURES

Figure		Page
3.1	Effect of Wax Content on Kinematic Viscosity of Refinery AC Samples	37
3.2	Effect of Wax Content on Kinematic Viscosity of Contractor AC Samples	38
3.3	Effect of Asphaltene Content on Kinematic Viscosity of Contractor AC Samples	39
A.1	NMR Spectra of Asphalt Cement Samples Nos. 1 and 8	54
A.2	NMR Spectra of Asphalt Cement Samples Nos. 5 and 12	55
A.3	NMR Spectra of Resinous Samples Nos. 1 and 8	56
A.4	IR Spectra of Asphalt Cement Sample No. 1	57
A.5	IR Spectra of Asphalt Cement Sample No. 5	58
A.6	IR Spectra of Asphalt Cement Sample No. 10	59
A.7	IR Spectra of Asphalt Cement Sample No. 14	60
A.8	NMR Spectra of Wax Extracted from Sample No. 2	61
A.9	NMR Spectra of Wax Extracted from Sample No. 6	62
A.10	NMR Spectra of Wax Extracted from Sample No. 10	63
A.11	NMR Spectra of Wax Extracted from Sample No. 13	64
A.12	GLC Chromatograms of Wax Extracted from Sample No.1	65
A.13	GLC Chromatograms of Wax Extracted from Sample No.8	66

CHAPTER 1

INTRODUCTION

Performance data for several roadway pavement sections have clearly indicated that both functional and structural failures as well as poor service qualities could be attributed to the use of asphalt cements manufactured from Western Desert crudes in either the construction or maintenance of these pavements. Furthermore, laboratory evaluation of Western Desert asphalt cements conducted in the last decade showed that the product was not homogeneous and the wax content varied between approximately 5 and 15% (Metwally et al., 1975).

Western Desert crude oils are processed in the refineries of El-Nasr Petroleum Company in Alexandria, where paving grades of asphalt cements are produced by propane deasphalting, dewaxing, and phenol extracting processes. The crude oils reaching the refineries are not secured from specific fields, but are rather mixtures of different crude oils. The main producing oil fields in the Western Desert are Abu-El-Gharadig, El-Alamein, Yadama, Razzak, and Mobarka (for more details, the reader is referred to TAP Report 80-4).

The primary objective of this study is to establish the basic chemical and physical properties of local asphalt cements produced from the Western Desert crude oils. Also, the study investigates the variability in the properties of asphalt

cements produced from different Western Desert crude oil batches reaching the refinery over a considerable length of time. The check-variability concept was extended to investigate the variation that may occur in the properties of asphalt cements produced from the same batches, but stored for some time in one of the road construction companies.

This report presents the results of the study performed to establish the fundamental properties of the 60/70 asphalt cement penetration grade produced by the Alexandria refineries during the period of September to December 1979. The 60/70 penetration grade of asphalt cement is widely used in most paving operations in Egypt. Crude oils employed in producing some of the investigated asphalt cement batches are also included in the study.

The report includes the results of tests performed on check samples secured from a road construction company (contractor). These asphalt cement samples were manufactured from the same crude oil batches and over the same period of time as the first refinery samples. The results of these samples are needed to substantiate the findings obtained from the refinery samples and/or to check the effect of storage on the various chemical and physical properties of Western Desert 60/70 asphalt cement penetration grade.

The first section of this report deals with the sampling plan and the experimental design of the study, together with

a description of the testing program performed according to international and/or local standard procedures. Test results on the crude oils, the refinery, and the contractor asphalt cement samples are then presented. An evaluation and discussion of the results of each group of samples, along with a comparison between the refinery and contractor samples are given. The last section includes the main conclusions of this study.

CHAPTER 2

SAMPLING PLAN AND EXPERIMENTAL DESIGN OF THE STUDY

2.1 Sampling Plan

2.1.1 Refinery Asphalt Cement Samples

Two samples of the 60/70 penetration grade asphalt cement (AC 60/70), a barrel each, were secured weekly from the El-Nasr Petroleum Company for 12 weeks (during the period from September to December, 1979), bringing the total to 24 samples. Each batch* in the refinery was sampled by the El-Nasr Company only once and relevant data about the batch were filed in the refinery for further use. At the end of each week, the two asphalt cement samples were sent to the El-Nasr Petroleum Company headquarters in Cairo, and then delivered to the research team. These samples were divided between the Egyptian Petroleum Research Institute (EPRI) and the Road Research Laboratory (RRL) for the proposed chemical and physical testing programs, respectively. The work performed in this program was planned, coordinated, and supervised by the Cairo University (CU) research team.

2.1.2 Contractor Asphalt Cement Samples

Asphalt cement samples (AC 60/70) produced by El-Nasr Petroleum Company in Alexandria were also secured from a

---

*The crude oil reaches the refinery in batches. The batches consist of a mixture from different fields.

road construction company (contractor). These samples were produced by the refinery during the same period as the previous samples (September - December, 1979). Nine barrels were randomly selected from the stock of the 60/70 asphalt cement grade stored by the contractor. Each barrel was sampled twice, bringing the total number of samples to eighteen. Necessary information was recorded on each sample container and samples were subjected to the same testing program as the refinery samples. The only difference between the contractor and refinery samples is the storage time. Testing the contractor samples started approximately two to three months after completion of the same testing program on the refinery samples.

2.2 Design of Experiments

The experiments utilized in this study were statistically designed to permit an objective analysis of the important factors affecting the performance of asphalt cements.

2.2.1 Refinery Samples

Standard statistical analysis, such as the determination of the mean, standard deviation, and coefficient of variation, were performed for the 24 samples. In addition, regression analyses were conducted to evaluate possible relationships between the different measured properties.

2.2.2 Contractor Samples

The main objective of this phase of the investigation is to evaluate differences between batches and the effect of storage time on the asphalt cement properties. In addition, the variation in properties within the barrel is also evaluated. Two samples were therefore obtained from the nine barrels obtained from the contractor: one sample from the surface and one from the middle. Tests were conducted on the eighteen samples.

A fixed two-way (9×2) completely randomized design (Anderson and Mclean, 1974) with one observation per cell is utilized in this phase of the study to evaluate the batch and the sample position effects. The model is as follows:

$$Y_{ij} = \mu + \beta_i + P_j + \beta P_{ij} + \varepsilon_{(ij)} \qquad (2.1)$$

where:

$i = 1,\ldots,9 \qquad j = 1,2$

Y_{ij} = the measured property

μ = overall mean

β_i = the effect of the ith batch (fixed)

P_j = the effect of the jth sample position (fixed)

βP_{ij} = interaction effect

$\varepsilon_{(ij)}$ = experimental error, zero df, NID $(0,\sigma^2)$

The interaction effects, βP_{ij}, and the error effects, $\varepsilon_{(ij)}$, are confounded due to the fact that only one observation

per cell was performed. The test for the batch and position effects was performed by assuming that the interaction βP is zero. However, a technique given by Tukey (1949) was used to split the sum of squares of the βP and/or error term into one portion for the βP term (nonadditivity) which has one degree of freedom and the remaining portion for the error term.

2.2.3 Comparison Between Refinery and Contractor Samples

The main objective of this phase is to investigate, statistically, the difference between the means of the two samples (refinery and contractor samples). This was conducted through the use of a "two-sample t-test." Prior to the difference between means test, the hypothesis of equality of sample variations was investigated by the F-test.

The t-test is not overly sensitive to small differences between the sample variances. However, when the difference between the sample variances turned out to be significant, i.e., it is unreasonable to treat the sample variances as being equal, the "two-sample t-test" cannot be used. A modified test procedure, the "t'-test", as described by Ostle (1969) was used herein when the F-test showed a significant difference. The t'-test is believed to be a reasonable approximation to the t-test.

In addition, two options were used in this phase:

(1) When the effect of sample position (surface vs middle) proved insignificant, the "two-sample t-test" was performed between the overall contractor sample (18 observations) and the refinery sample (24 observations).

Alternatively,

(2) When the effect of sample position proved significant, the contractor samples were treated as two different groups (surface and middle) each of which contains 9 observations. Each group was then tested separately against the refinery samples.

2.3 Testing Procedures

The chemical and physical properties tests conducted on both the refinery and contractor samples are shown in Table 2.1 together with the procedures followed. In addition, test results on some Western Desert crude oil batches were provided by El-Nasr Petroleum Company.

Test Property	Procedure
Component analysis	
• Asphaltenes	IP 143
• Oils and Resins	El-Fayoumy (1975)
Neuclear magnetic resonance (NMR)	Ramsey, et al.
Gas liquid chromotography (GLC)	Marquart, et al. (1966)
Infrared analysis	Bellamy (1975)
Penetration, 100 gm, 5 sec., 25°C	ASTM D5
Ductility, cm, 25°C	ASTM D113
Kinematic viscosity, C.St., 135°C	ASTM 2170
Absolute viscosity, Poises, 60°C	ASTM D2171
Flash point (cleveland-Open-Cup), C°	ASTM D92
Softening point (ring-and-ball), C°	ASTM D36
Thin-Film-Oven Test (TFOT)	ASTM D1754

Table 2.1 - Asphalt Cement Tests and their Procedures

CHAPTER 3

TEST RESULTS

3.1 Crude Oil Properties

Properties of crude oil are of primary importance because of their effect on the characteristics of asphalt cements. In the study of crude oils, the properties of the residual fractions were emphasized.

Table 3.1 presents the main physical and chemical characteristics of some of the major oil-producing fields in the Western Desert (Technology Adaptation Program, 1980). In general, the Western Desert crude oils are characterized by their significantly high wax and low sulfur contents. Furthermore, the properties of the crudes vary from one oil field to the other. For example, the crude oil recovered from the El-Alamein field has significantly higher carbon, sulfur, and wax contents than the others.

Table 3.2 shows the physical and chemical characteristics of the curde oil batches received by the Alexandria refinery during August to October, 1979. The data in this table were provided by the El-Nasr Petroleum Company. The results in Table 3.2 clearly indicate that the batches are uniform and that the crudes have relatively high sulfur content and specific gravity. Considering the techniques used in the refinery and the uniform nature of the blends, results in Table 3.2 suggest that asphalts produced from these crudes

should also be uniform with minor variations in their properties.

A component analysis of the Western Desert crude oils was performed on the high boiling fractions (above 300°C). This analysis provides information on the quantitative distribution of the different components forming the crude oils. Based on the results in Table 3.3, the Western Desert crudes can be classified according to the Carpatica method (Creanga, 1961) as paraffinic-naphthenic of the waxy-resinous-sulfurous or non-sulfurous group. Therefore, unless a special treatment is carried out, the asphalt cements produced from these crudes are expected to have the same characteristics.

3.2 Asphalt Cement Properties

3.2.1 Refinery Asphalt Cement Samples

Chemical Properties - Table 3.4 presents the results of the component analysis performed on the 24 asphalt cement samples obtained from the Alexandria refinery.

The analysis indicates that, in all samples, the main constituents are: resins (46-61%); followed by oils (25-35%); and finally, asphaltenes (13-20%). With the exception of two samples (7 & 9), the resins represent more than 50%, and hence are considered to be relatively high at the expense of oils rather than asphaltenes. Furthermore, all the 24 samples are characterized by a relatively high wax content (6-8%).

The component analysis results also indicate that the asphalt cement samples secured from the Alexandria refinery were not, most probably, produced by straight-run distillation only. They were rather obtained as blends of straight-run fractions, resins, and asphaltenes extracted during lubricating oil solvent refining processes. If straight-run distillation were only used in producing these asphalt cements from the crude batches having the chemical properties described previously, these asphalts would have had much higher oil and wax contents than those obtained in the 24 samples.

Nuclear magnetic resonance (NMR) spectral techniques were used to study the chemical nature of some asphalt samples and their resinous components. The results are summarized in Tables 3.5 and 3.6. These results indicate that the paraffinic proton types represent the major part of the whole protons, while the aromatic protons are the minor types proving the paraffinic nature of the asphalt and even the paraffinic nature of the resins themselves.

In addition, typical NMR spectra figures (Figs. A.1 through A.3 in Appendix A) clearly show that all the bands associated with the aromatic protons appeared in the spectra as broad and diffused ones. In most cases, they could only be identified by the integration curves. The low intensity of the aromatic protons indicates mainly high substituted rings and/or high condensed structures.

The infrared spectral analysis was also performed on the asphalt cement samples (Figs. A-4 through A-7). The results indicate complete similarity between these asphalt cement samples.

Chemical Analysis of the Wax - Results of NMR spectral analysis of the paraffinic wax are shown in Table 3.7 and presented in Figs. A.8 through A.11 in Appendix A.

The results show no aromatic protons, which indicates that aromatic contaminants are not present. Also, very few branching could be detected and the main bulk of the wax is primarily normal paraffin with some naphthenic hydrocarbons or isoparaffins.

Further chemical tests on the wax component employing the gas liquid chormatographic analysis (Figs. A-12, A-13) proved that the wax is mainly composed of normal paraffinic hydrocarbons (C_8 to C_{28}) with some traces of either iso- or cycloparaffins.

Physical Properties - Table 3.8 shows the results of the physical tests performed on the refinery asphalt cement samples. Table 3.9 presents the existing and proposed Egyptian standard specifications for the local asphalt cement (AC60/70).

Test results shown in Table 3.8 indicate that the samples generally satisfy the existing standard specifications for this asphalt cement grade. The high flash point is consistent with the low light fraction content. The kinematic viscosity is remarkably low (239 - 378 c.st.) and reflects, to a certain degree, the paraffinic nature of the asphalt cement. Only one sample achieved the proposed kinematic viscosity standard (320 c.st.).

Figure 3.1 illustrates the relationship between the wax content and kinematic viscosity of the refinery samples. No clear trend can be detected because of the narrow range of wax content variation in the samples tested (approximately 6 and 8%). A more pronounced effect of wax content on viscosity is expected for greater variations in wax contents.

Linear regression analyses performed to establish relationships between different properties of the refinery asphalt cements indicate very low coefficients of correlations.

3.2.2 Contractor Asphalt Cement Samples

Nine AC 60/70 barrels were secured from a contractor. Each barrel was sampled twice: one sample was taken from the surface and the other from the middle in order to study the effect of storage time on these properties.

Chemical Properties - Results of the component analysis for the eighteen samples are shown in Table 3.10, together

with the mean ($\bar{x}$), the standard deviation (s), and coefficient of variation (c.v.,%).

Physical Properties - The main physical properties of the contractor samples before and after the thin-film-oven test, TFOT, are shown in Tables 3.11 and 3.12 for the surface and middle samples, respectively. Also, the calculated mean, standard deviation, and coefficient of variation are included in these tables.

Comparing the results of the physical tests to the standard specifications (Table 3.9), three middle samples and one surface sample do not comply with the penetration specification limits. All the other properties satisfy existing Egyptian standard specifications. However, the kinematic viscosity of all samples are below the proposed limit (320 c.st.; Table 3.9).

The effect of wax and asphaltene contents on the kinematic viscosity of the two groups of samples are shown in Figs. 3.2 and 3.3. As discussed previously, because of the narrow range of wax content variation in the samples, no clear trend can be detected between wax content and kinematic viscosity. On the other hand, Fig. 3.3 shows that the asphaltene content is slightly correlated to the kinematic viscosity. This is particularly more pronounced for middle rather than for surface samples.

Characteristic	Abu El Gharadig		El-Alamein	Razzak
	I	II		
API gravity	34.5	37.9	31.7	38
Carbon content, wt %	2.18	2.15	4.67	2.74
Pour point, °C	7.0	6.0	10.0	7.2
Sulfur content, wt %	0.46	0.36	1.14	0.86
Water content, %	0.25	0.15	nill	0.05
Asphaltenes, wt %	0.29	0.19	4.5	1.89
Ash content, wt %	0.013	0.005	0.03	0.01
Wax content, wt %	4.84	3.72	8.40	3.48
A.S.T.M., IP. Dist. Initial boiling point, °C	46	41	55	54
% Recovered at 75°C	3	4	1	5
at 100°C	5	8	5.0	10
at 125°C	12	14	10	17
at 150°C	19	21	15.5	25
at 175°C	25	28	21	31
at 200°C	30	34	27	36
at 225°C	35	40	32	42
at 250°C	40	45	38	47
at 275°C	45	50	42	52
at 300°C	51	55	47	58

Table 3.1 - General Physical and Chemical Characteristics of Some Western Desert Crude Oils

Tests \ Sample No.	1	2	3	4	5	6	7	8
Specific gravity at 20°C	0.828	0.8265	0.8269	0.8252	0.8280	0.8264	0.8271	0.8262
Water content, vol. %	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Sulfur content, wt. %	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Salt content, wt. %	0.002	0.003	0.003	0.003	0.002	0.002	0.003	0.002
ASTM Distillation								
Initial boiling point, C°	54	54	54	54	52	51	51	51
% Recovered at 100°C	11	11	11	11	11	11	11	11
% Recovered at 125°C	19	19	19	19	18.5	19	19	19
" " 150°C	25	25	25	25	25	25	25	25
" " 175°C	33	33	33	33	32	32	32	32
" " 200°C	38	38	38	38	37	37	37	37
" " 225°C	45	45	45	45	44	44	44	44
" " 250°C	49	49	49	49	49	49	49	49
" " 275°C	55	55	55	55	55	55	55	54
" " 300°C	61	61	61	61	61	61	61	61

Table 3.2 - Chemical and Physical Characteristics of Western Desert Crude Oil Mixtures (Alexandria Refinery, Aug.-Oct. 1979)

Component	Abu El-Gharadig		El-Alamein	Razzak	Yadama	Mobarka
	I	II				
Distillate up to 300°C, %	51.40	55.60	42.30	50.9	57.2	50.8
Asphaltenes, %	0.29	0.19	4.5	1.89	4.4	0.7
Oils, %	30.94	33.94	32.3	43.40	33.2	40.1
Resins, %	16.97	13.97	19.9	3.8	5.2	8.4

Table 3.3 - Component Analysis of Western Desert Crude Oils

Sample	Wax, %	Resins, %	Asphaltenes, %	Oils,%
1	5.86	58.27	16.95	24.66
2	6.73	54.65	18.98	26.05
3	6.01	51.24	19.66	28.89
4	7.01	53.71	17.19	28.91
5	7.27	54.64	18.19	26.97
6	6.71	50.97	18.97	29.74
7	6.19	46.03	19.45	34.43
8	6.08	53.57	17.71	28.57
9	7.00	47.98	17.39	34.54
10	6.82	53.64	17.98	28.20
11	7.17	65.27	17.41	26.12
12	7.41	53.49	13.96	32.00
13	7.94	54.41	13.49	32.07
14	6.37	51.97	17.53	30.32
15	7.07	58.17	15.02	26.73
16	6.47	60.66	16.79	25.52
17	7.51	56.68	14.74	28.46
18	7.28	58.19	15.01	28.73
19	6.59	56.41	14.70	28.69
20	7.70	53.03	15.01	31.81
21	7.24	56.78	15.19	28.00
22	7.13	55.63	14.79	29.56
23	6.79	58.82	14.38	26.79
24	6.86	58.17	13.45	28.36
$\bar{X}$*	6.88	55.10	16.41	28.9
s**	0.536	4.08	1.952	2.586
cv*** (%)	7.79	7.40	11.9	8.94

* Mean - ** Std. Deviation - *** Coefficient of Variation

Table 3.4 - Component Analysis of Refinery Samples

Proton Type	Asphalt Sample No.			
	1	5	8	12
CH3	18.0	17.4	18.4	17.2
CH2	57.1	59.6	56.9	57.8
CH	22.2	19.0	71.4	71.1
Aromatics	2.7	4.0	3.5	3.9

Table 3.5 - Per Cent Proton Types Distribution in Some AC Refinery Samples

Proton Types	Resinous Sample No.	
	1	8
CH3	16.5	21.5
CH2	55.3	53.8
CH	21.5	18.0
Aromatics	6.7	6.7

Table 3.6 - Per Cent Proton Types Distribution in Two Resin Samples

Proton Type	Sample No.			
	2	6	10	13
CH3	3.70	3.78	3.27	2.81
CH2	20.25	19.96	20.68	21.41
CH	1.00	1.35	1.04	0.78
Aromatics	-	-	-	-

Table 3.7 - Per Cent Proton Type Distribution-NMR Spectroscopy of Wax

Sample No.	Before T.F.O.T.						After T.F.O.T.			
	Pen., 0.1mm	Duct., cm	Kin. Visc. 135°C, c.st.	Abs. Visc. 60°C, poises	Flash pt., C°	Soft pt., C°	Pen.*, %	Duct., cm	Visc. 135°C c.st.	Abs Visc. 60°C poises
1	64	> 150	260	1,113	324	52.5	66.4	> 150	336	2,662
2	65	> 150	247	1,047	321	52.5	63.8	> 150	329	2,284
3	63	> 150	247	998	312	51.0	69.8	> 150	329	2,241
4	64	> 150	246	971	315	51.5	64.1	> 150	353	2,616
5	63	> 150	239	902	320	50.5	70.6	> 150	293	1,968
6	64	146	250	1,017	320	52.5	67.2	144	340	2,750
7	67	123	257	1,107	305	54.0	66.4	80	358	3,805
8	66	149	257	1,089	322	53.5	65.2	105	363	3,254
9	62	> 150	264	1,212	308	53.0	67.7	59	355	3,791
10	68	> 150	250	1,020	305	52.5	60.3	100	370	3,780
11	64	> 150	243	1,116	310	51.0	64.1	> 150	359	3,193
12	65	> 150	250	1,105	312	51.0	63.8	> 150	385	2,890
13	62	> 150	239	1,052	308	53.0	59.7	110	366	4,071
14	64	150	287	1,397	311	53.0	64.1	82	398	4,117
15	65	> 150	279	1,103	312	54.0	66.2	125	406	2,672
16	64	> 150	320	1,357	319	53.0	64.1	> 150	532	3,101
17	64	> 150	281	1,133	308	54.0	65.6	> 150	366	3,150
18	66	147	282	1,163	310	53.5	63.6	145	403	3,213
19	66	> 150	259	1,079	313	52.0	65.2	120	349	3,163
20	68	> 150	252	1,027	310	51.5	64.7	> 150	344	2,735
21	67	> 150	252	974	307	51.5	64.2	> 150	356	2,965
22	66	> 150	254	961	309	49.0	65.2	> 150	356	2,929
23	64	> 150	257	1,128	311	52.0	67.2	140	356	2,929
24	68	> 150	257	1,052	312	51.5	64.7	143	350	2,670
$\bar{x}$	64.96		259.64	1088.46	312.67	52.0	65.16		364.67	3039.54
s	1.78		18.45	113.83	5.50	1.242	2.43		43.37	560.81
C.V.	2.74		7.11	10.46	1.76	2.38	3.73		11.88	18.45

* % of original penetration

Table 3.8 Physical Characteristics of Refinery Asphalt Cement Samples

Test	Standard	Status
1. Penetration at 25°C, 100 gm, 5 sec.	60/70	Existing
2. Softeneing point (Ring-and-Ball), C°	45/55	
3. Ductility at 25°C, cm. min.	90	
4. Flash point (Cleveland-open-cup), C°(min)	250	
5. Kinematic viscosity, C.st., 135°C, min	320	Proposed

Table 3.9 - Existing and Proposed Egyptian Standard Specifications for the 60/70 pen. Asphalt Cement
(General Authority for Rural Roads)

No.	Surface Samples				Middle Samples			
	% wax	% oil	% resin	% asphal-tene	% wax	% oil	% resin	% asphal-tene
1	6	23.9	60.84	15.22	6.14	26.05	61.35	12.37
2	6.12	25.79	57.90	16.19	5.88	25.27	61.12	13.21
3	6.21	27.88	59.74	12.12	5.31	26.48	59.90	13.50
4	7.34	26.04	60.44	13.08	5.65	23.84	60.42	15.62
5	5.97	26.74	54.70	18.3	5.23	25.32	61.55	12.78
6	6.46	27.29	57.97	14.63	5.95	24.34	58.92	16.46
7	5.73	25.56	56.31	18.05	5.48	23.29	58.39	18.23
8	6.12	27.20	57.21	15.53	5.36	26.26	55.83	17.42
9	6.14	23.97	56.52	19.06	5.28	26.65	55.65	17.62
$\bar{x}$	6.23	26.04	57.96	15.8	5.59	25.28	59.24	15.25
s	0.459	1.412	2.05	2.367	0.333	1.21	2.25	2.30
C.V.%	7.37	5.42	3.54	14.98	5.97	4.8	3.80	15.11

Table 3.10 - Component Analysis of Contractor A.C. Samples

No.	Before T.F.O.T.						After T.F.O.T.			
	Pen. 0.1 mm.	Duct. cm	kin.visc. 135°C	Abs.visc. 60°	Flash.pt. °C	Sft.pt. °C	% pen	Duct. cm	Kin.visc. 135°C	Abs.vis. 60°C
1	67	>150	253	974	324	50.5	64.18	56	350	2,717
2	62	>150	256	1,009	326	50	62.9	100	340	2,527
3	63	>150	241	974	324	54	57.17	>150	315	2,251
4	62	>150	248	967	323	52.5	67.74	43	357	2,966
5	62	>150	203	774	318	52	75.81	>150	464	1,786
6	67	>150	249	969	324	52	65.67	>150	357	2,781
7	73	>150	259	993	326	49.5	61.64	>150	356	2,470
8	62	>150	201	1,111	317	53	67.74	>150	364	3,249
9	66	>150	201	1,081	318	52	63.64	>150	399	2,915
$\bar{x}$	64.89		234.56	983.56	322.22	51.72	65.17		356.89	2629.00
s	3.76		25.19	94.24	3.56	1.46	5.14		42.55	433.00
C.V. %	5.79		10.74	9.58	1.11	2.82	7.89		11.6	16.47

Table 3.11 - Physical Characteristics of Contractor A.C. Surface Samples

No.	Before T.F.O.T.						After T.F.O.T.			
	Pen., o.1mm	duct., cm	kin.visc. 135°C	Abs.visc. 60°C	Flash.pt. °C	Soft.pt. °C	Pen. %	Duct. cm	Kin.visc. 135°C	Abs.visc 60°C
1	68	> 150	233	937	323	51.5	63.2	>150	361	1,498
2	58	> 150	250	1,018	325	51.5	70.7	>150	329	2,139
3	57	> 150	241	929	324	52	73.7	>150	331	2,194
4	65	> 150	249	1,002	324	50	63.1	143	354	2,889
5	73	> 150	217	699	318	50	61.6	>150	290	1,779
6	67	> 150	259	992	325	50	62.7	>150	360	2,805
7	67	> 150	247	955	322	50	61.2	>150	336	4,072
8	63	> 150	262	1,158	325	50	65.1	>150	378	4,298
9	67	> 150	282	1,472	326	48	59.7	>150	383	3,733
$\bar{x}$	65		248.89	1018.00	323.56	50.33	64.56		347.00	2,823
s	5.02		18.39	208.225	2.4	1.2	4.65		28.77	1,017.19
C.V.%	7.73		7.39	20.45	0.74	2.38	7.20		8.29	36.03

Table 3.12 - Physical Characteristics of Contractor A.C. Middle Samples

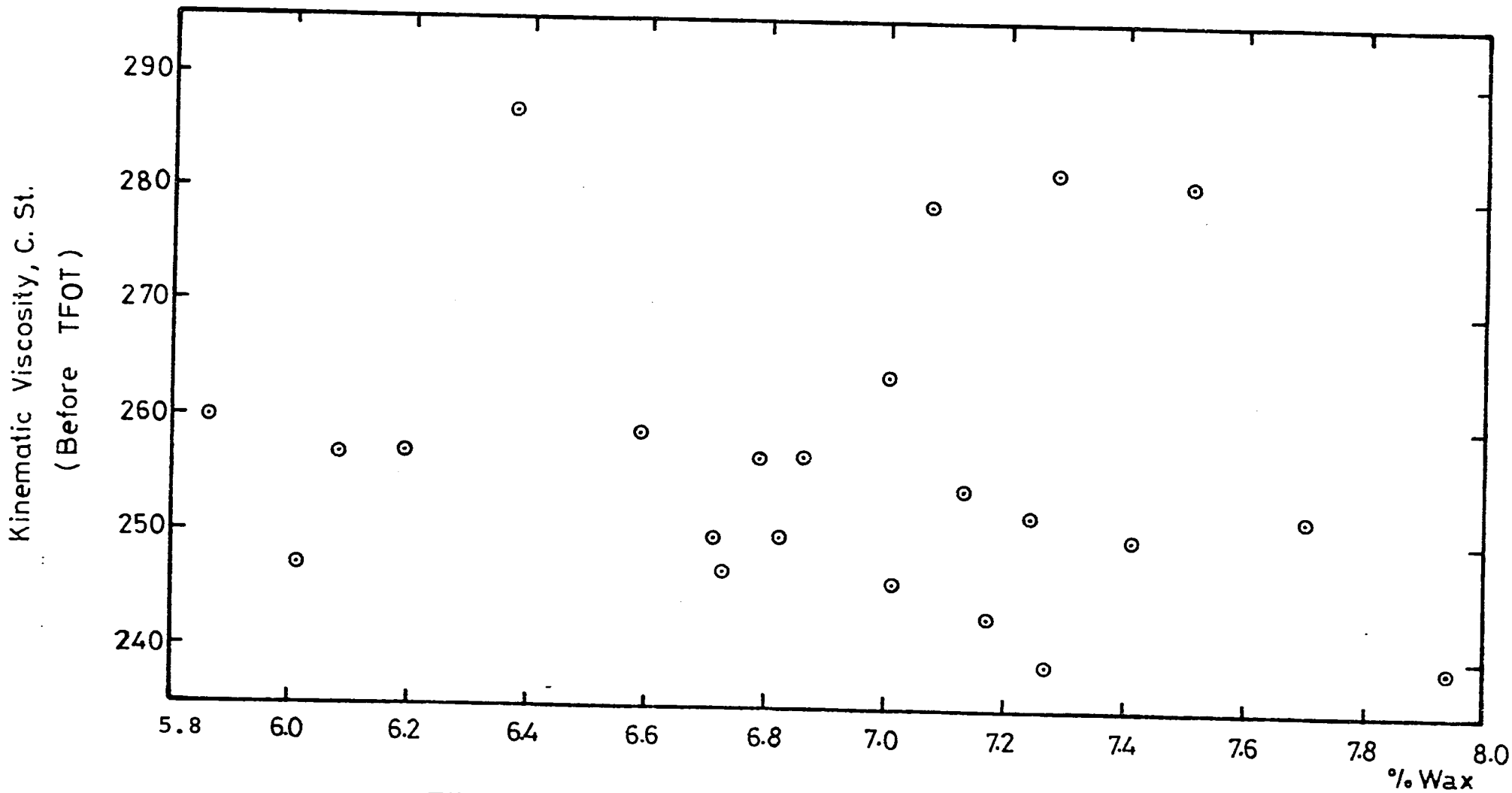

Fig. 3.1 – Effect of Wax Content on Kinematic Viscosity of Refinery AC Samples.

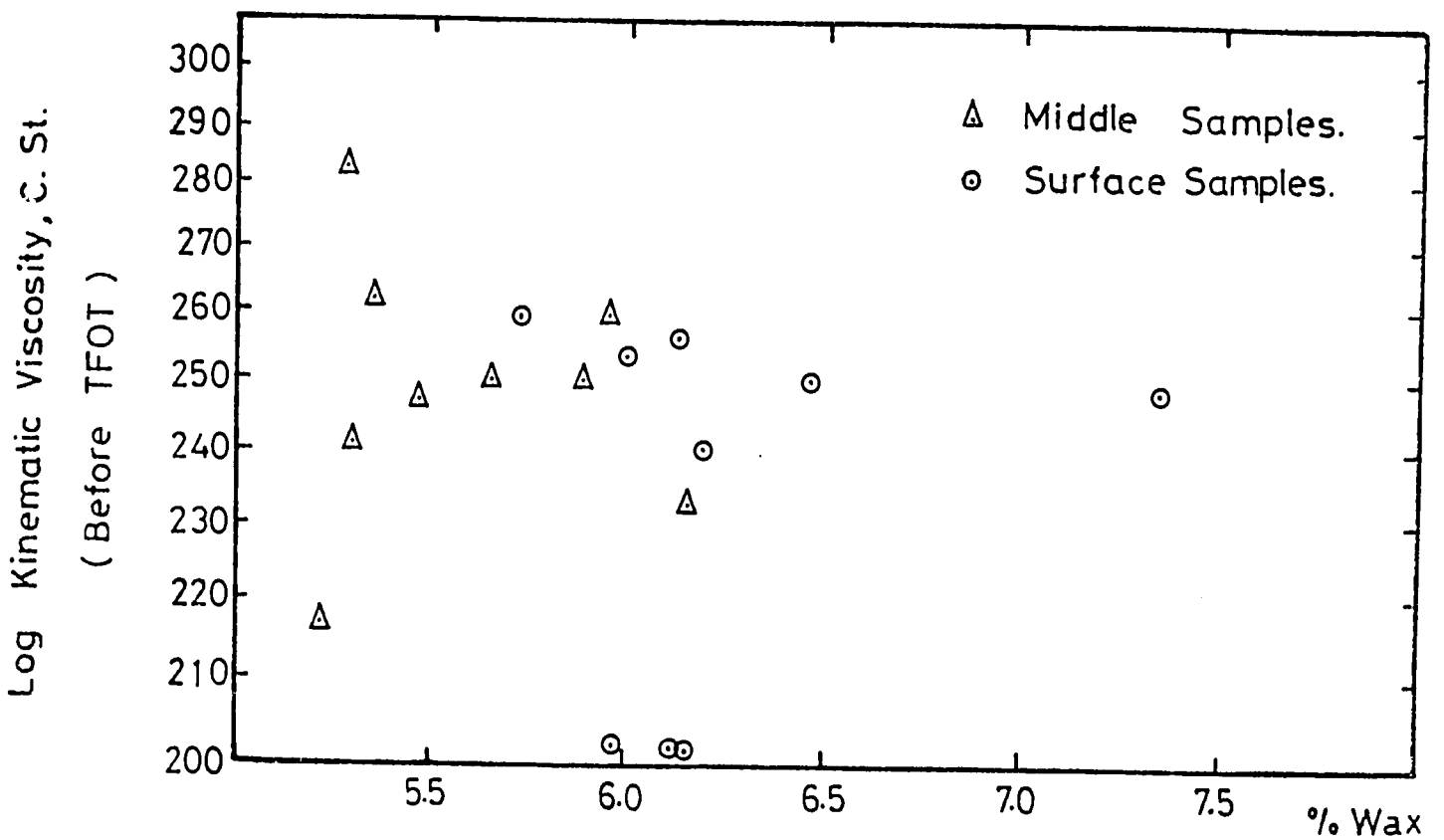

Fig. 3.2 -Effect of Wax Content on Kinematic Viscosity of Contractor AC Samples.

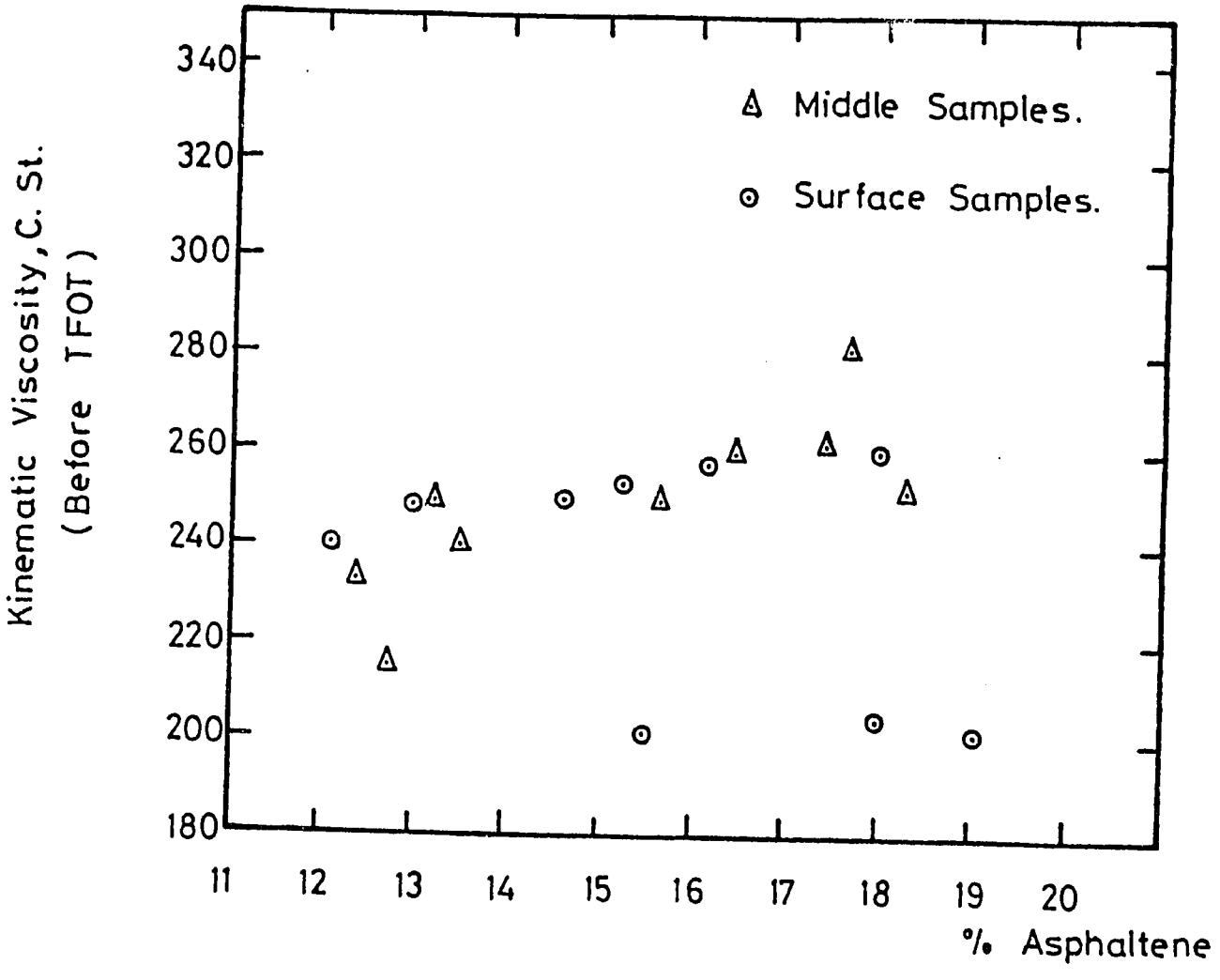

Fig. 3.3 - Effect of Asphaltene Content on Kinematic Viscosity of Contractor AC Samples.

CHAPTER 4

ANALYSIS OF RESULTS

4.1 Contractor Asphalt Cement Samples

Statistical analyses of the measured properties were conducted according to the model described earlier in Chapter 2 (Eq. 2.1). Table 4.1 represents a typical analysis of variance, ANOVA, table for one of the measured properties (kinematic viscosity before TFOT). A 5% level of significance ($\alpha = 0.05$) was utilized in the analysis of all the tested properties.

Table 4.2 summarizes the results of the analysis of variance of the test data. A study of the main effects and interactions indicates the following:

(1) The batch effect is not significant on most of the measured properties with the exception of the absolute viscosity before and after the thin film oven test and the wax content. This conclusion, however, should be viewed with some caution as the test results apply only to the inference space constituted by the contractor asphalt cement samples and testing methods used.

(2) The effect of sample location (surface vs middle) on properties is not significant except for the wax content. Surface samples have a slightly higher wax content, possibly caused by the migration

of wax towards the surface of the barrel during storage.

(3) The interaction effect (nonadditivity) between the batch (B) and position (p) is not significant in most of the measured properties (see Table 4.2), with the exception of the absolute viscosity before and after TFOT, penetration after TFOT and wax content. This indicates that the interaction term (BP) could have been deleted from the model when dealing with these properties.

4.2 Comparison Between the Refinery and Contractor Asphalt Cement Samples

Laboratory test results on asphalt cement samples obtained from the refinery and from the surface and the middle of contractors' barrels show differences. Table 4.3 shows the mean, the standard deviation, and the coefficient of variation of the various physical and chemical properties of the three groups of samples: 24 refinery; 9 contractor (surface); and 9 contractor (middle).

An indication of hardening that occurred in the contractor samples is evident from the results in Table 4.3. The average flash point of these samples is higher than that of the refinery samples (323°C and 313°C , respectively). Also, the average oil per cent of the contractor samples is 2.86 to 3.6%, depending on the sample location, less than that of refinery samples, while the average resin per cent shows a

reversed trend. This indicates that oil fractions had changed to resins which is coupled, as may be expected, with a decrease in the average oil content of the contractor samples.

However, the evaluation of the significance of the variation between these three groups of samples is a difficult task and depends on the objectives of this evaluation. For practical applications in pavement construction, the differences in properties in Table 4.3 are considered to be small based on engineering judgment of experts. This is supported by the fact that all properties of all three gorups of samples satisfy the Egyptian standard specifications (Table 3.9), with the exception of:

(1) The wax content.

(2) The kinematic viscosity, which is the main property of practical significance that is affected by the high wax content of the waxy asphalt cements.

A more systematic variability study based on well-established statistical methods is performed below. In evaluating these results, it is important to note that statistical analyses depend on the choice of the level of significance, expressed by the parameter α. The choice of the value of α depends on the application and can be controversial. The following results are based on $\alpha = 5\%$ typically used in many applications.

Table 4.4 summarizes the results of the "tests of difference between means" for the properties of the refinery and contractor samples. The means and variances are based on 24 and 18 test values for the refinery and contractor samples, respectively. However, due to the significant difference in wax content between the two contractor sample groups (surface and middle), each group is tested separately against the refinery samples.

The statistical tests (Table 4.4) reveal significant differences, at a significant level of 5%, between the refinery and contractor samples in the following properties: kinematic and absolute viscosities (before TFOT), softening point, per cent wax, per cent oil, and per cent resins. The last three properties showed the highest variations.

Source of Variance	Degree of freedom	Sum of squares	Mean squares	F	F critical	Significance
Batch (B_i)	8	3,128.2	391.03	< 1	3.73	N.S.*
Position (P_j)	1	924.5	924.50	1.54	5.59	N.S.
BP_{ij} (nonadditivity)	1	446.8	446.80	< 1	5.59	N.S.
Error $\varepsilon_{(ij)}$	7	4,208.2	601.17			
Total	17	8,707				

* N.S. = not significant at $\alpha = 0.05$

Table 4.1 - Typical Analysis of Variance Table (Kinematic viscosity, before TFOT)

Property		Factor (Source of Variation)		
		Batch effect (B) n = 9	Position effect (P) surface vs. middle	Interaction effect (BP)
Physical	Penetration	N.S.*	N.S.	N.S.
	Kinematic visc.	N.S.	N.S.	N.S.
	Absolute visc.	S**	N.S.	S
	Softening point	N.S.	N.S.	N.S.
	After TFOT			
	Penetration	N.S.	N.S.	S
	% Penetration	N.S.	N.S.	N.S.
	Kinematic visc.	N.S.	N.S.	N.S.
	Absolute visc.	S	N.S.	S
Chemical	% wax	S	S	S
	% Oil	N.S.	N.S.	N.S.
	% Resins	N.S.	N.S.	N.S.
	% Asphaltenes	N.S.	N.S.	N.S.

Note: * N.S.=not significant at $\alpha = 0.05$

** S. =Significant at $\alpha = 0.05$

Table 4.2 - Summary of Analysis of Variance; Contractor Samples

Sample Group		Statistical Property	CHEMICAL CHARACTERISTICS				PHYSICAL CHARACTERISTICS							
							BEFORE T.O.F.T.					AFTER T.O.F.T.		
			% Wax	% Oil	% Resin	% Asphaltene	PEN, 0.1 mm	Kin Visc @ 135°C	Abs Visc @ 60°C	Flash Pt °C	Soft Pt °C	% PEN	Kin Visc @ 135°C	Abs Visc @ 60°C
Refinery Samples (n=24)		$\bar{x}$ (1)	6.88	28.90	55.10	16.41	64.96	259.64	1088.46	312.67	52.00	65.16	364.67	3039.54
		s (2)	0.54	2.59	4.08	1.95	1.78	18.45	113.83	5.50	1.242	2.43	43.37	560.81
		cv (%) (3)	7.79	8.94	7.40	11.90	2.74	7.11	10.46	1.76	2.38	3.73	11.88	18.45
Contractor Samples	Surface-barrel (n=9)	$\bar{x}$	6.23	26.04	57.96	15.80	64.89	234.56	983.56	322.22	51.72	65.17	366.89	2629.00
		s	0.46	1.41	2.05	2.37	3.76	25.19	94.24	3.56	1.46	5.14	42.55	43.3.00
		cv (%)	7.37	5.42	3.54	14.98	5.79	10.74	9.58	1.11	2.82	7.89	11.60	16.47
	Middle-barrel (n=9)	$\bar{x}$	5.59	25.28	59.24	15.25	65.00	248.89	1018.00	323.56	50.33	64.56	347.00	2823.00
		s	0.33	1.21	2.25	2.30	5.02	18.39	208.225	2.40	1.20	4.65	28.77	1017.19
		cv (%)	5.97	4.8	3.80	15.11	7.73	7.39	20.45	0.74	2.38	7.20	8.29	36.03

(1) $\bar{x}$ = mean (2) s = standard deviation (3) cv = coefficient of variation = mean/standard deviation

Table 4.3 Summary of Physical and Chemical Properties of Refinery and Contractor Samples

	Property	Equality of Variance Test		Difference between Mean Test*	
		F calculted	Significance	t calculated	Significance
Physical	Penetration	5.84	S	0	N.S.
	Kinematic Viscosity	1.5	N.S.	2.83	S
	Absolute Viscosity	1.92	N.S.	2.08	S
	Softening point	1.42	N.S.	2.38	S
	After TFOT				
	Penetration	2.19	N.S.	0	N.S.
	% Penetration	3.18	S	0.28	N.S.
	Kinematic Viscosity	1.4	N.S.	0.63	N.S.
	Absolute Viscosity	1.85	N.S.	1.53	N.S.
Chemical	% Oil	4.43	S	4.36	S
	% Resins	2.51	N.S.	4.15	S
	% Asphaltene	1.36	N.S.	1.36	N.S.
	% Wax**				
	- Surface	1.36	N.S.	3.22	S
	- Middle	2.59	N.S.	6.71	S

S = Significant at $\alpha = 0.05$

N.S.= Not significant at $\alpha = 0.05$

* If the difference between the sample variances is significant, the t' test is used

** In statistical analyses, contractor samples are considered as one group except for the wax content where a significant difference between surface and middle barrel samples exists.

Table 4.4 - Test of Difference Between Refinery and Contractor Samples

CHAPTER 5

SUMMARY AND CONCLUSIONS

This report presents the results of an intensive study to establish the basic chemical and physical properties of local asphalt cements produced from the Western Desert crude oils. Two samples, a barrel each, of asphalt cement 60/70 penetration grade were secured weekly from the Alexandria refineries for 12 weeks, bringing the total to 24 samples. The samples were divided between the Egyptian Petroleum Research Institute and the Road Research Laboratory for an extensive chemical and physical testing program.

In order to provide a check on the quality of the samples obtained from the refineries, 18 additional samples were secured from a road construction company (contractor). Nine samples were recovered from the surface of nine separate barrels randomly selected and the remaining nine, from the middle of the barrels. These asphalt cement samples were produced from the same crude oil batches and over the same period of time as the 24 refinery samples described above. The tests conducted on the 18 samples from the contractor were performed to substantiate the findings obtained from the refinery samples and to investigate the effect of storage on the various chemical and physical properties.

In addition, test results on eight Western Desert crude oils batches reaching the Alexandria refineries between

August and October 1979 were provided by El Nasr Petroleum Company (refinery).

The results of this study show that:

Western Desert Crudes

(1) Tests performed on Western Desert crude oil batches reaching the Alexandria refinery during August to October 1979 indicate that the crude has uniform chemical and physical properties. Except for the El-Alamein field, the Western Desert crude oils are characterized by their low asphaltene, resin, and sulfur contents and high oil and wax contents.

(2) According to the Carpatica method, the crude oils of the Western Desert fields can be classified as paraffinic-naphthenic of the waxy-resinous-sulfurous or non-sulfurous group.

Asphalt Cement Samples Secured from Refinery

(1) Refinery asphalt cement samples (60/70 pen) grade are of a paraffinic nature and have a relatively high wax content (6-8%). The chemical analysis of these samples indicates that these asphalts were probably prepared by blending the asphalt produced by straight-run distillation with resins and asphaltenes extracts obtained from lubricating oil production.

(2) Nuclear magnetic resonance spectral techniques, gas liquid chromatographic, and infrared analyses clearly identify the paraffinic nature of the refinery asphalt cement

samples and even the paraffinic nature of their resins.

(3) The physical properties of refinery asphalt samples generally satisfy existing Egyptian standard specifications. However, flash points were relatively high indicating the considerable low content of light fractions.

(4) The kinematic viscosity of refinery samples is low (239-278 C.St.). Only one of the 24 samples satisfied the 320 C.St. minimum kinematic viscosity proposed in the Egyptian specifications.

Asphalt Cement Samples Secured from Contractor

(1) All contractor's samples (18) satisfied existing Egyptian standard specifications with the exception of three mid-barrel and one surface-barrel samples that did not comply with the penetration limits.

(2) As in the case of the refinery samples, the kinematic viscosity of all contractors samples are below the 320 C.St. limit proposed in the Egyptian specifications.

(3) A statistical analysis indicates that the batch effect on properties of various contractor's samples is not significant. The only significant effect is in the absolute viscosity (before and after TFOT) and in the wax content using a level of significance $\alpha = 5\%$.

(4) The effect of sample location (surface vs. mid-barrel) on properties is not significant except for the wax content. Surface samples have a slightly higher wax content,

possibly caused by the migration of wax during storage. The wax migration phenomenon was also observed in pavements.

(5) The kinematic viscosity is weakly correlated to the asphaltene content. The effect is more pronounced for mid-barrel samples.

(6) The properties of the contractors' samples show some deviations from the results on the refinery samples. Based on engineering judgment, these differences are believed to be small for practical applications in pavement construction. A more detailed statistical analysis shows that for a level of significance $\alpha = 5\%$, the contractor and refinery samples exhibit a significant difference in Kinematic and absolute viscositie (before TFOT), softening point, per cent wax, per cent oil and per cent resins.

REFERENCES

1. Anderson, V.L. and R.A. McLean, "Design of Experiments: A Realistic Approach," Marcel Dekker, Inc., New York, 1974.

2. ASTM Standards, American Society for Testing and Materials, 1976.

3. Bellamy, L.G., "The IR Spectra of Complex Molecules," Chapman and Hall, London, 3rd edition, 1975.

4. Creanga, C., "Studu Si Cercetari de Chimi," Acad. R.P.R., IX, 1, 193, 1961.

5. El-Fayoumy, G.F., "A Study on the Hydrocarbons of Some Local Crude Oils," Ph.D. thesis, Faculty of Science, Cairo University, 1975.

6. General Authority of Rural Roads, "Egyptian Standards for Paving Materials," Ministry of Transportation.

7. Institute of Petroleum, IP Standards for Petroleum and Its Products, Parts 1 and 2, London, 1971.

8. Marquart, J.R., G.B. Dellow, and E.R. Freitas, "Determination of Normal Paraffins in Heavy Gas Oils," Analytical Chemistry, 40, 11, 1633, 1966.

9. Metwally, S. et al., "Flexible Pavements Paraffinic Asphalt Cements," XVth World Road Congress, Mexico, 1975.

10. Ostle, B., "Statistics in Research," The Iowa State University Press, Ames, Iowa, USA, 1969.

11. Ramsey, J.W., F.R. McDonald, and J.C. Laromie, "A Structural Study of Asphalts by NMR," Petroleum Research Center, Bureau of Mines, U.S. Dept. of the Interior.

12. Technology Adaptation Program, "Performance of Paraffinic-Waxy Asphalt Cements in Egyptain Road Construction: Literature Review and Background of the Problem in Egypt," Vol. I, 1980.

13. Tukey, J.W., Biometrics, 1949.

APPENDIX A

TYPICAL CHARTS: CHEMICAL ANALYSIS

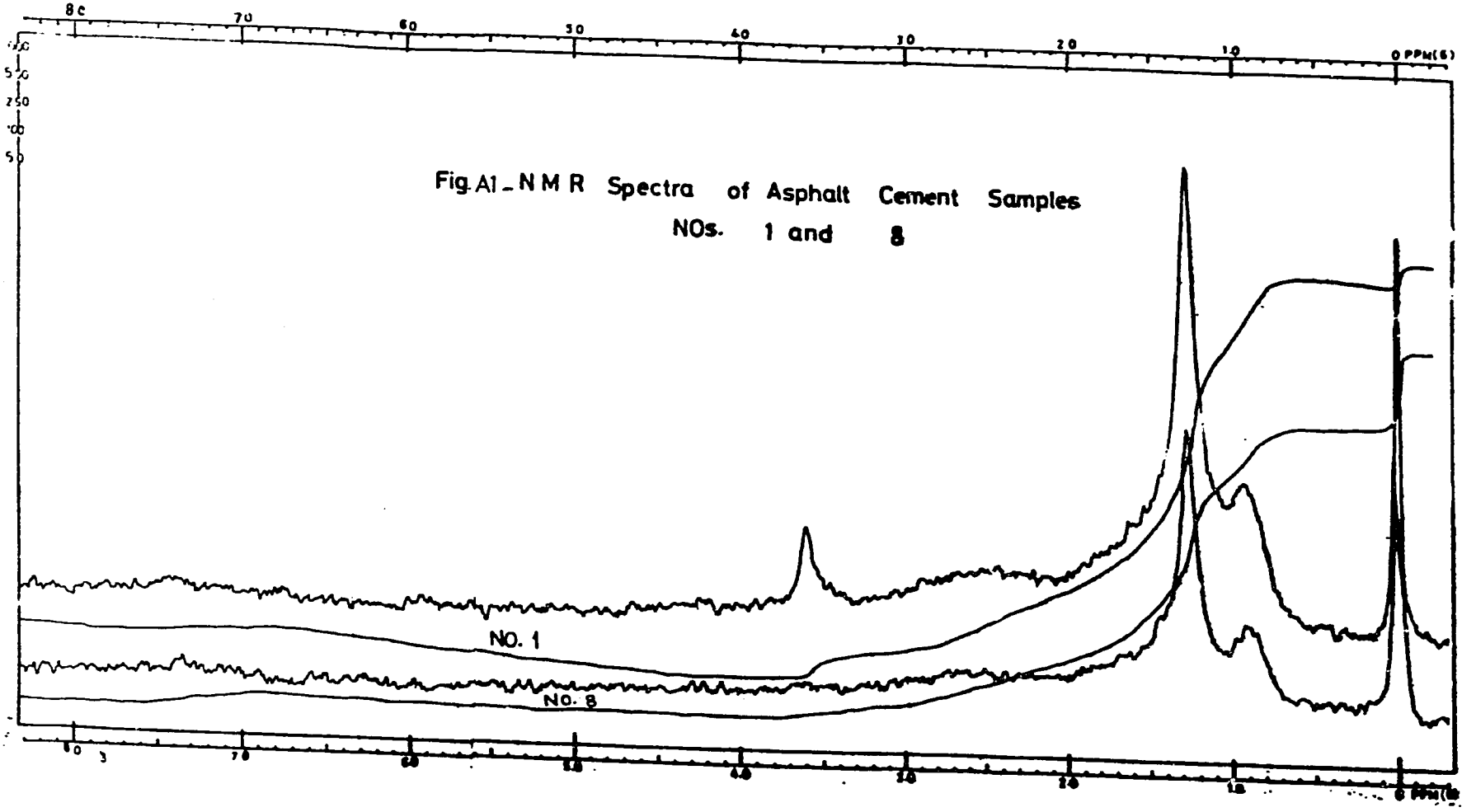

Fig. A1 – N M R Spectra of Asphalt Cement Samples NOs. 1 and 8

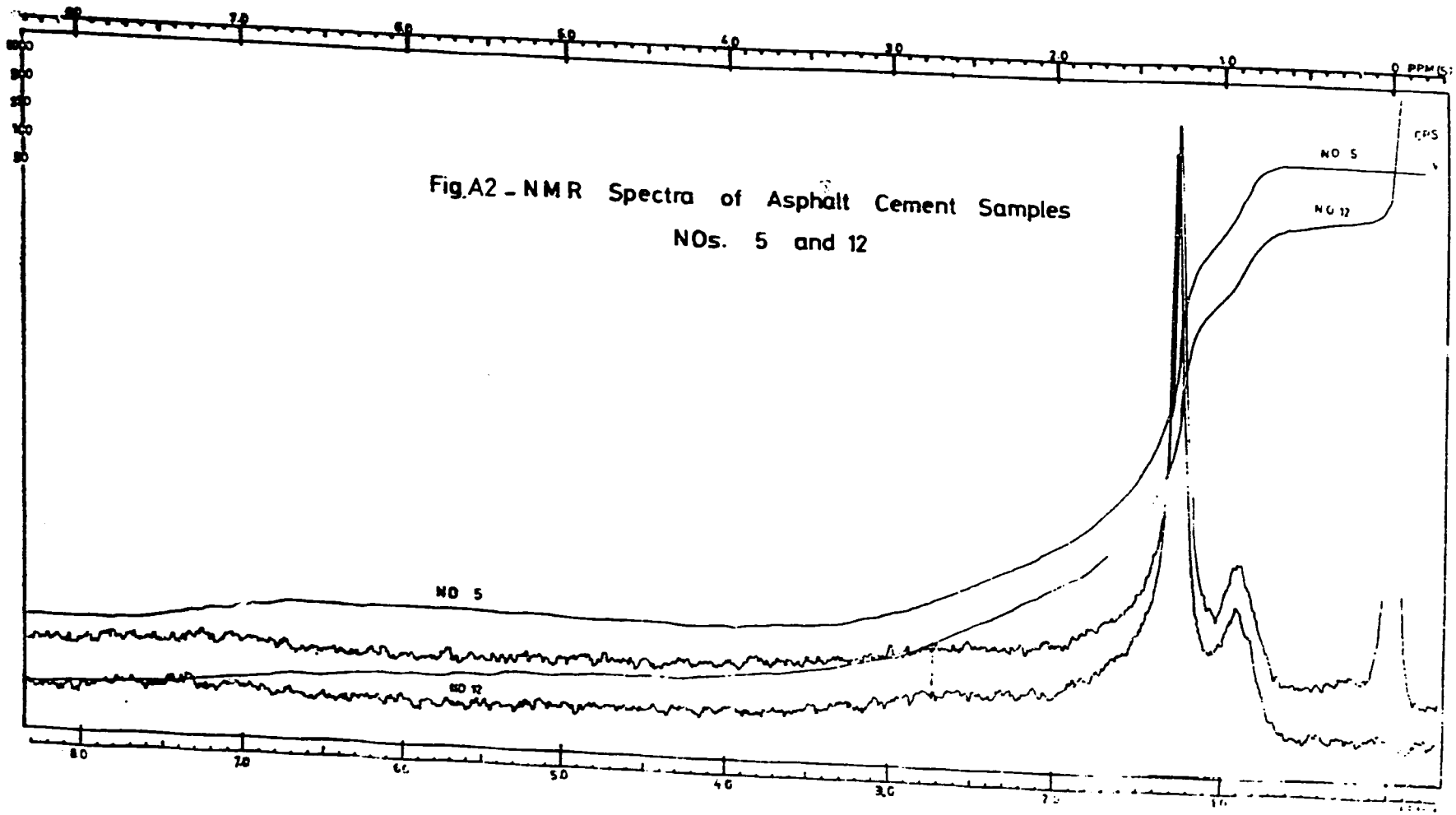

Fig.A2 - N M R Spectra of Asphalt Cement Samples
NOs. 5 and 12

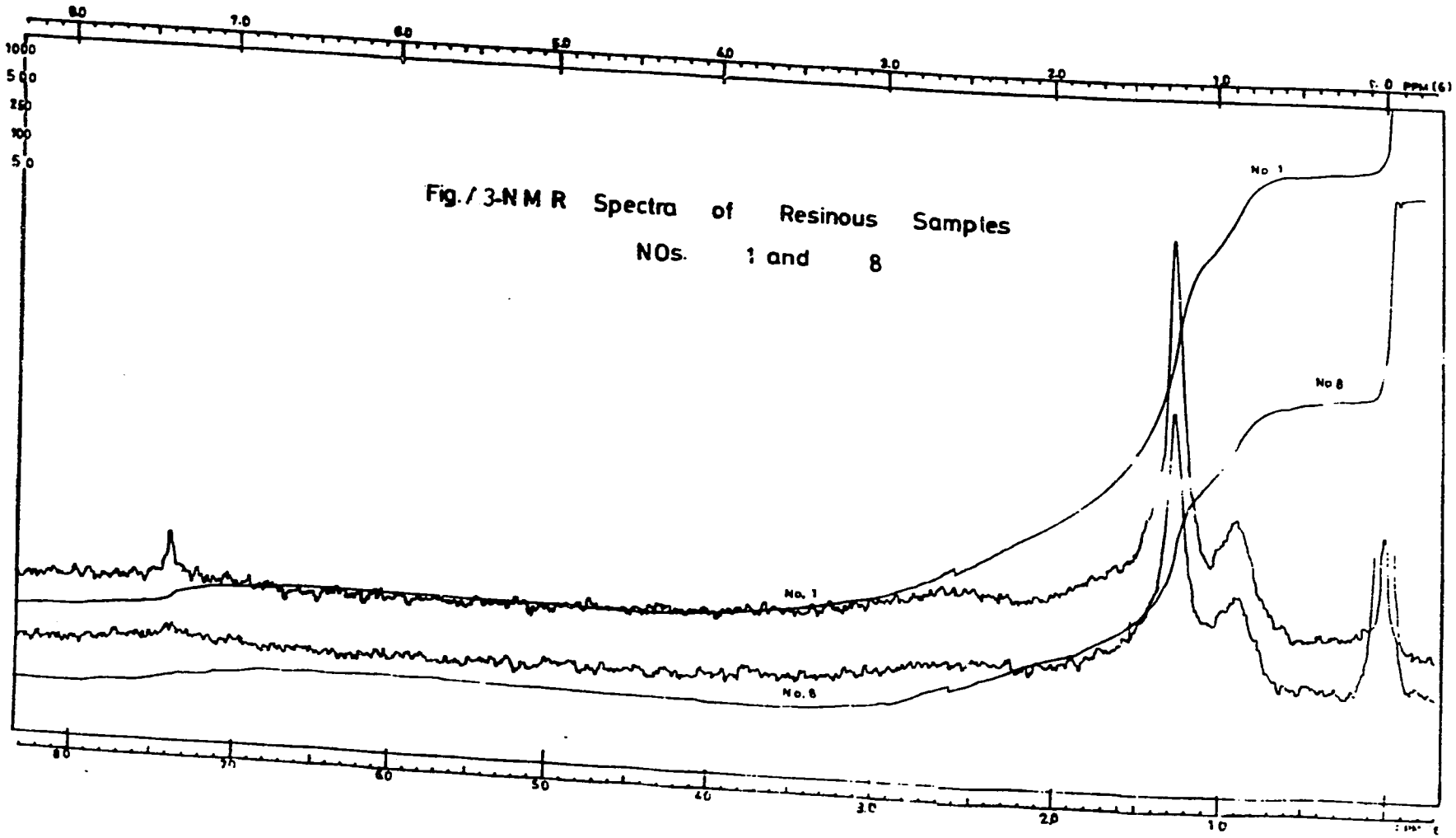

Fig. / 3-N M R Spectra of Resinous Samples NOs. 1 and 8

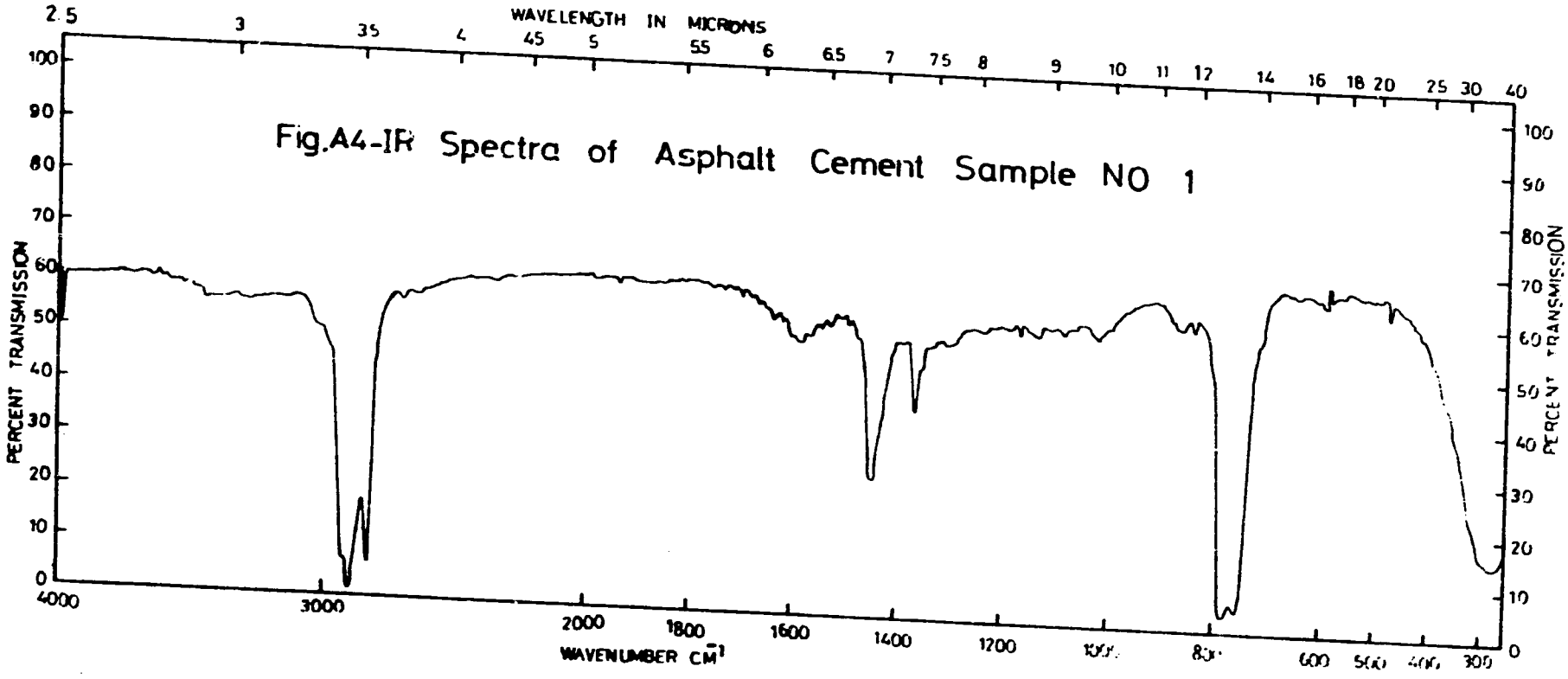

Fig.A4-IR Spectra of Asphalt Cement Sample NO 1

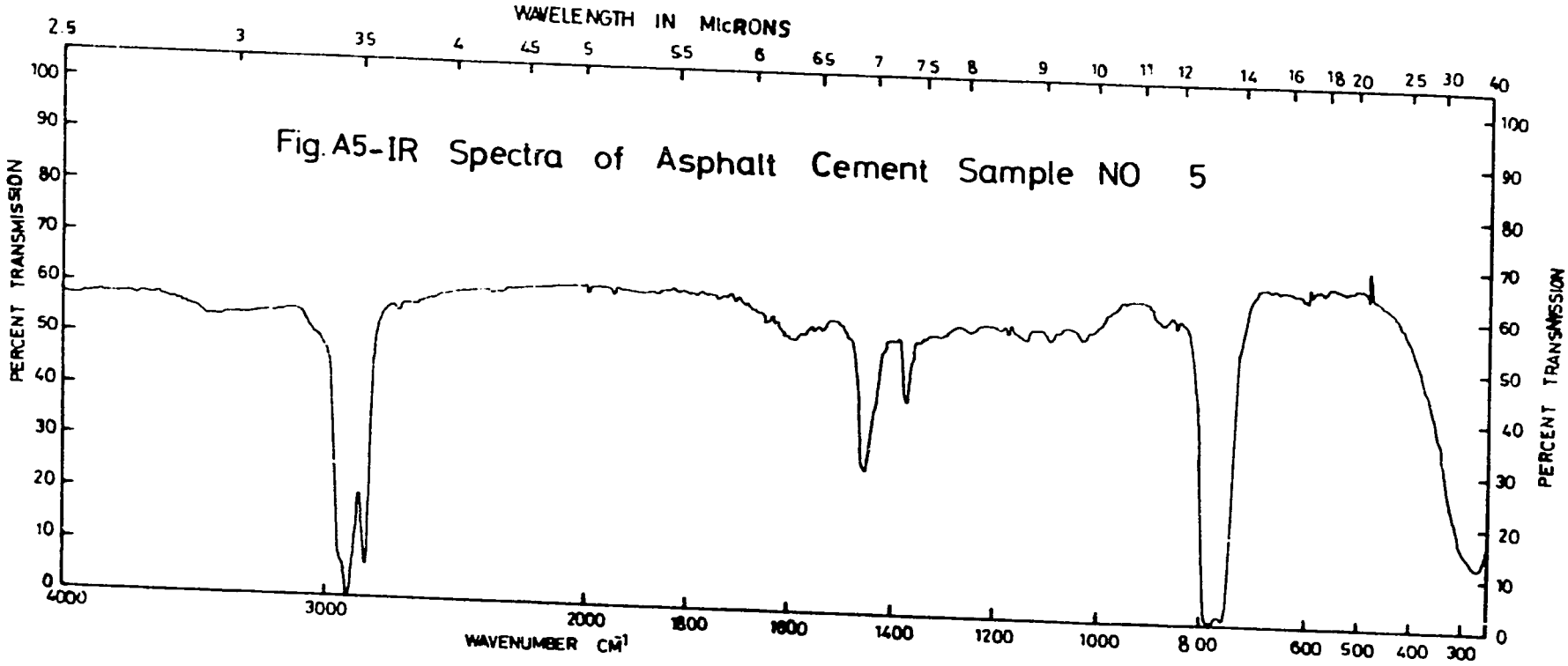

Fig. A5-IR Spectra of Asphalt Cement Sample NO 5

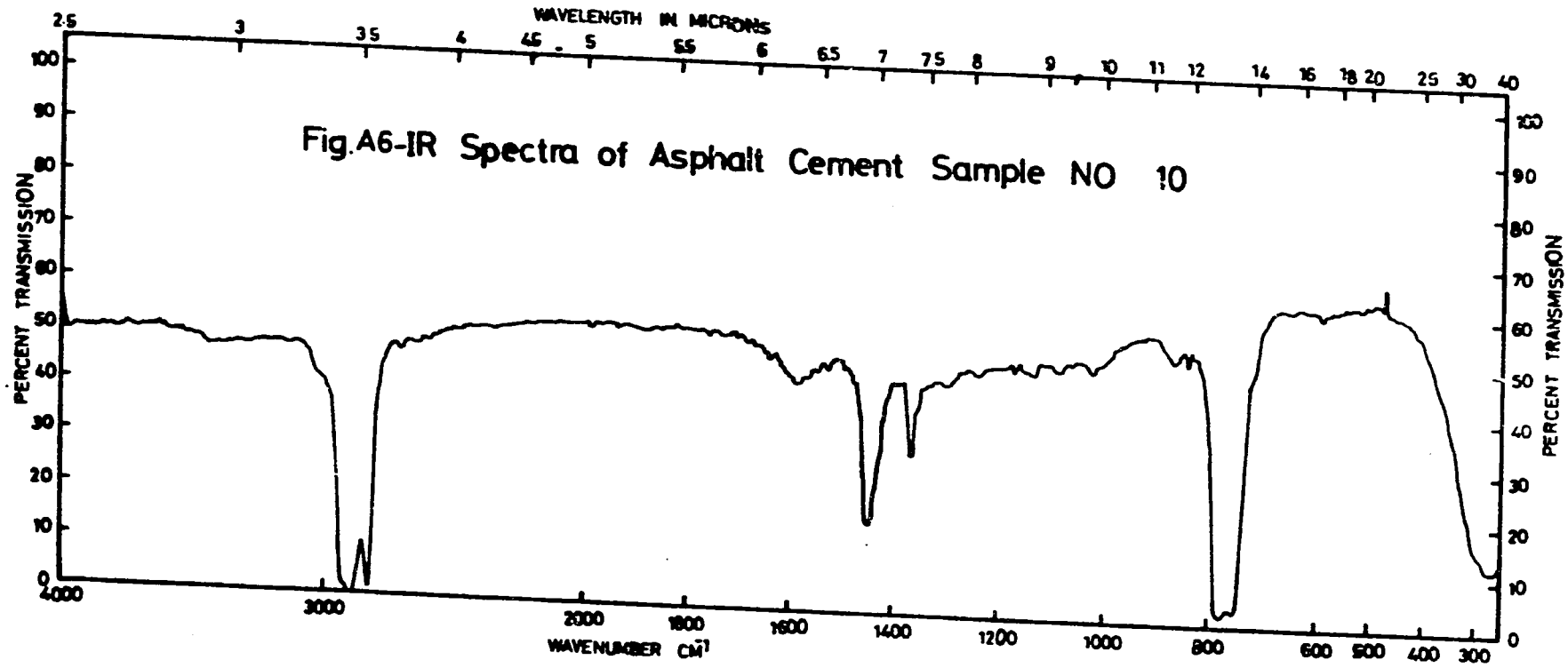

Fig.A6-IR Spectra of Asphalt Cement Sample NO 10

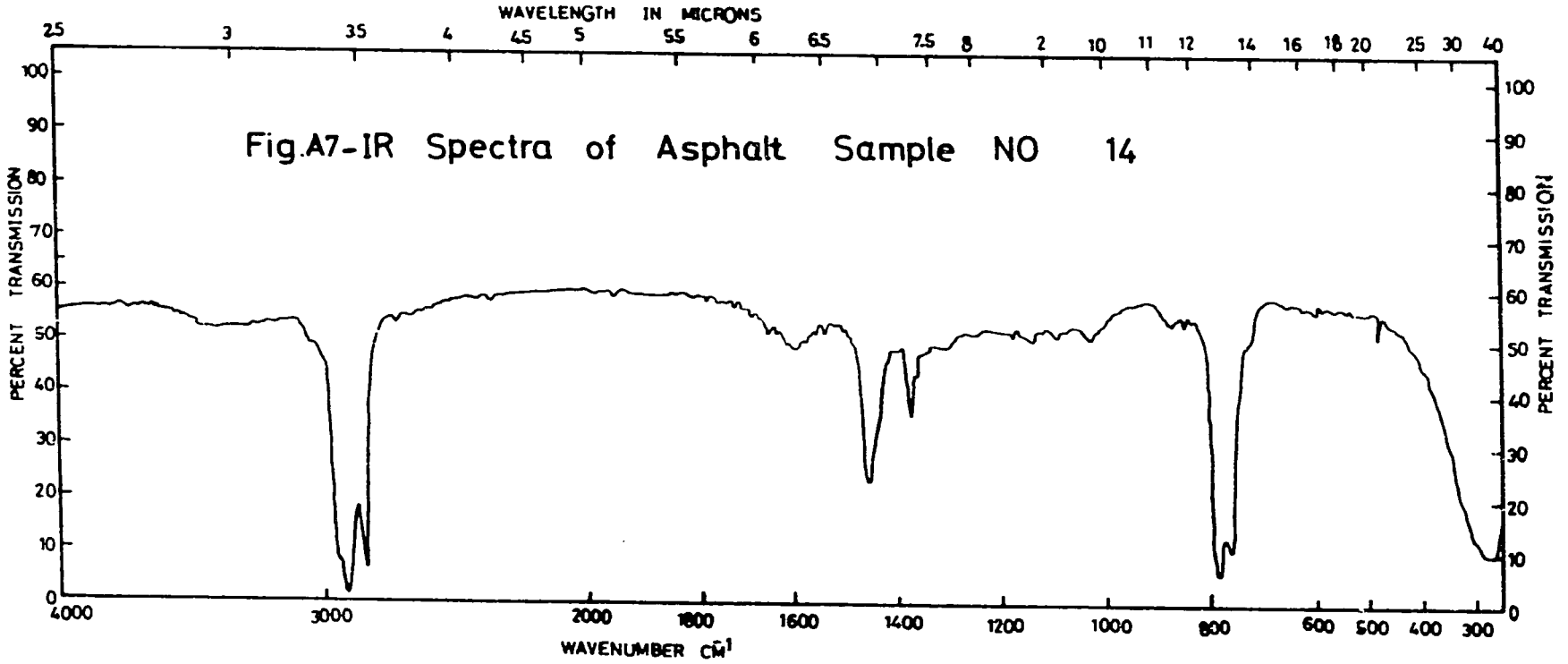

Fig.A7-IR Spectra of Asphalt Sample NO 14

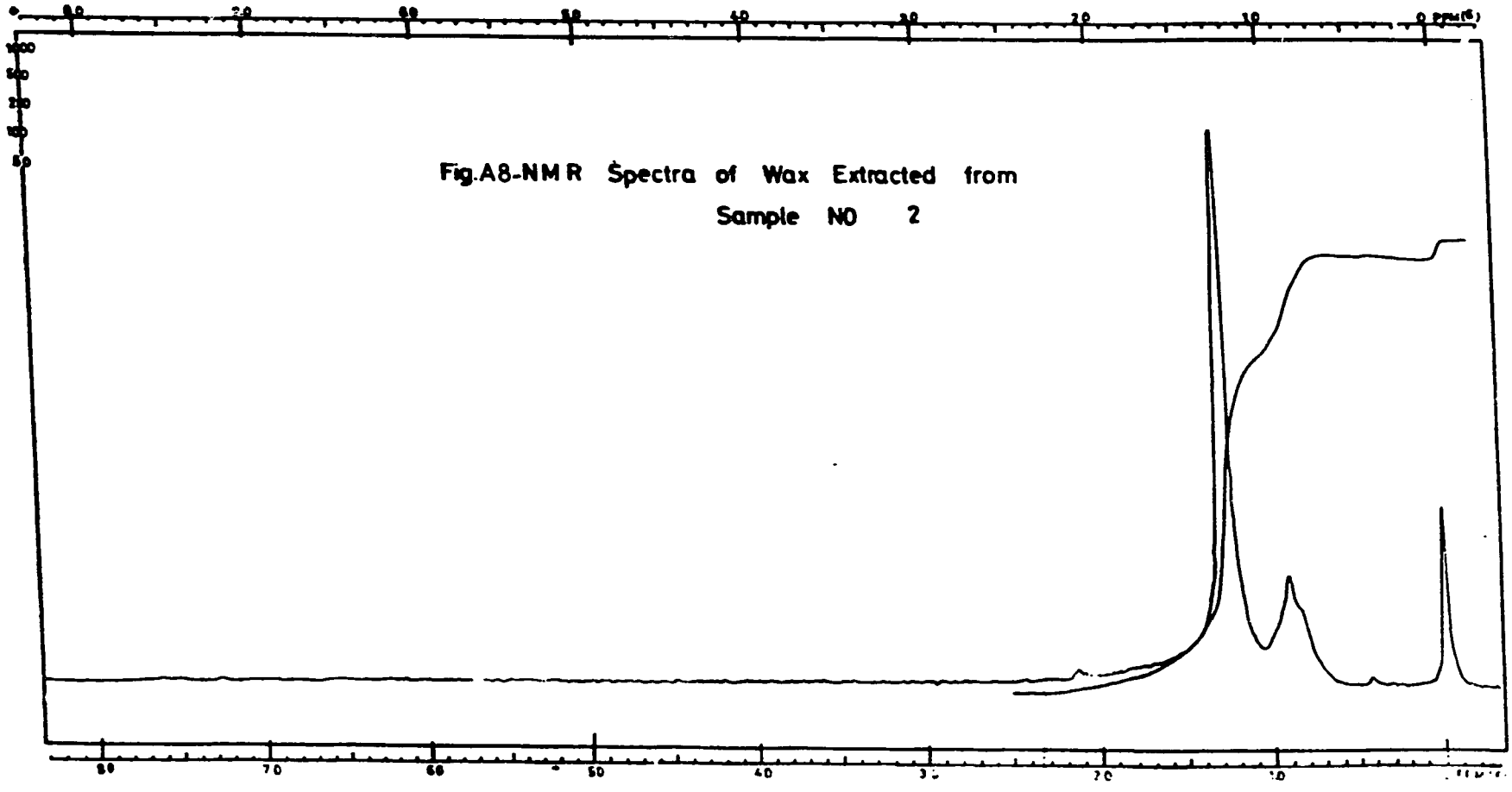

Fig.A8-NMR Spectra of Wax Extracted from Sample NO 2

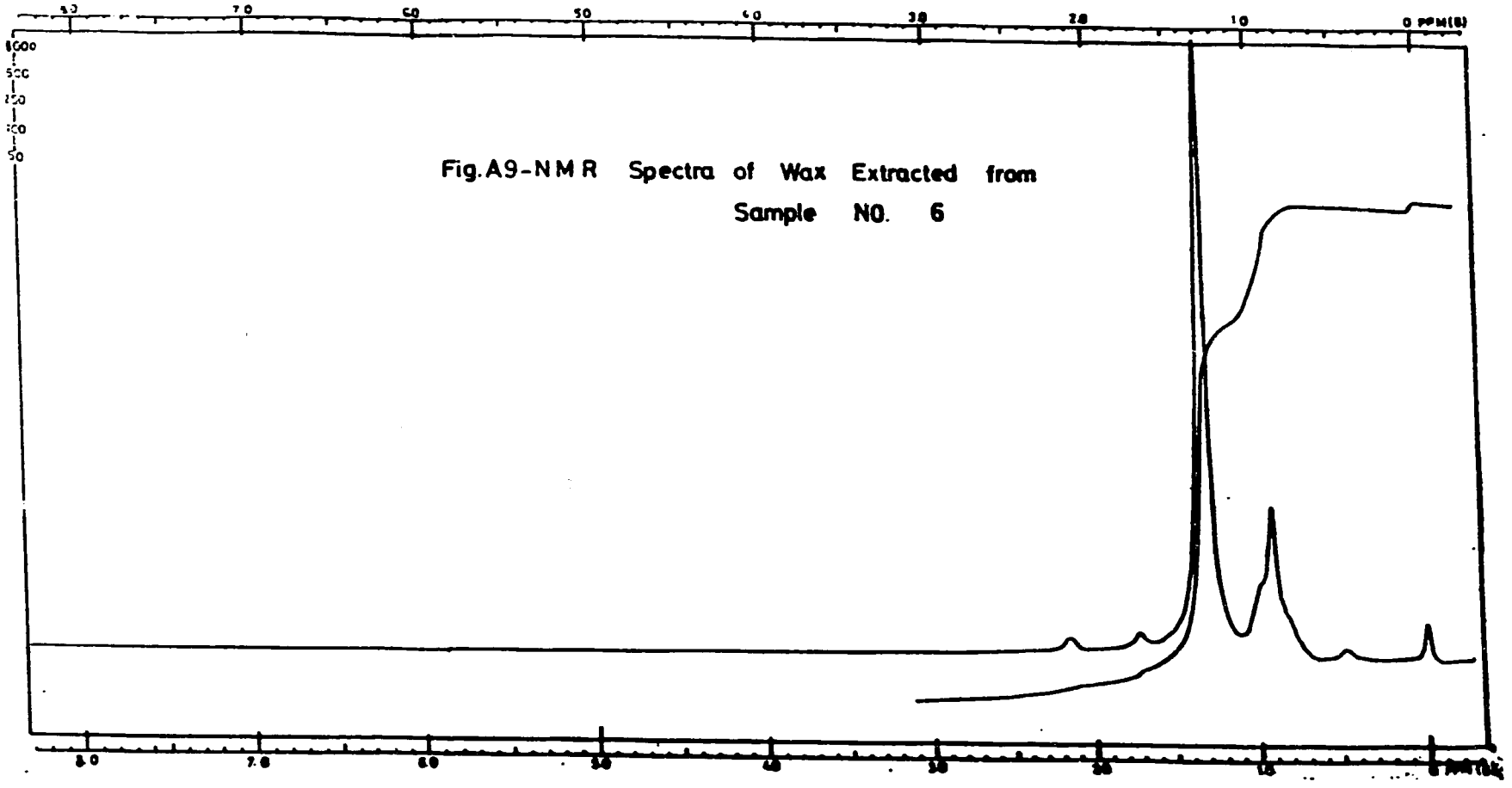

Fig. A9-N M R Spectra of Wax Extracted from Sample NO. 6

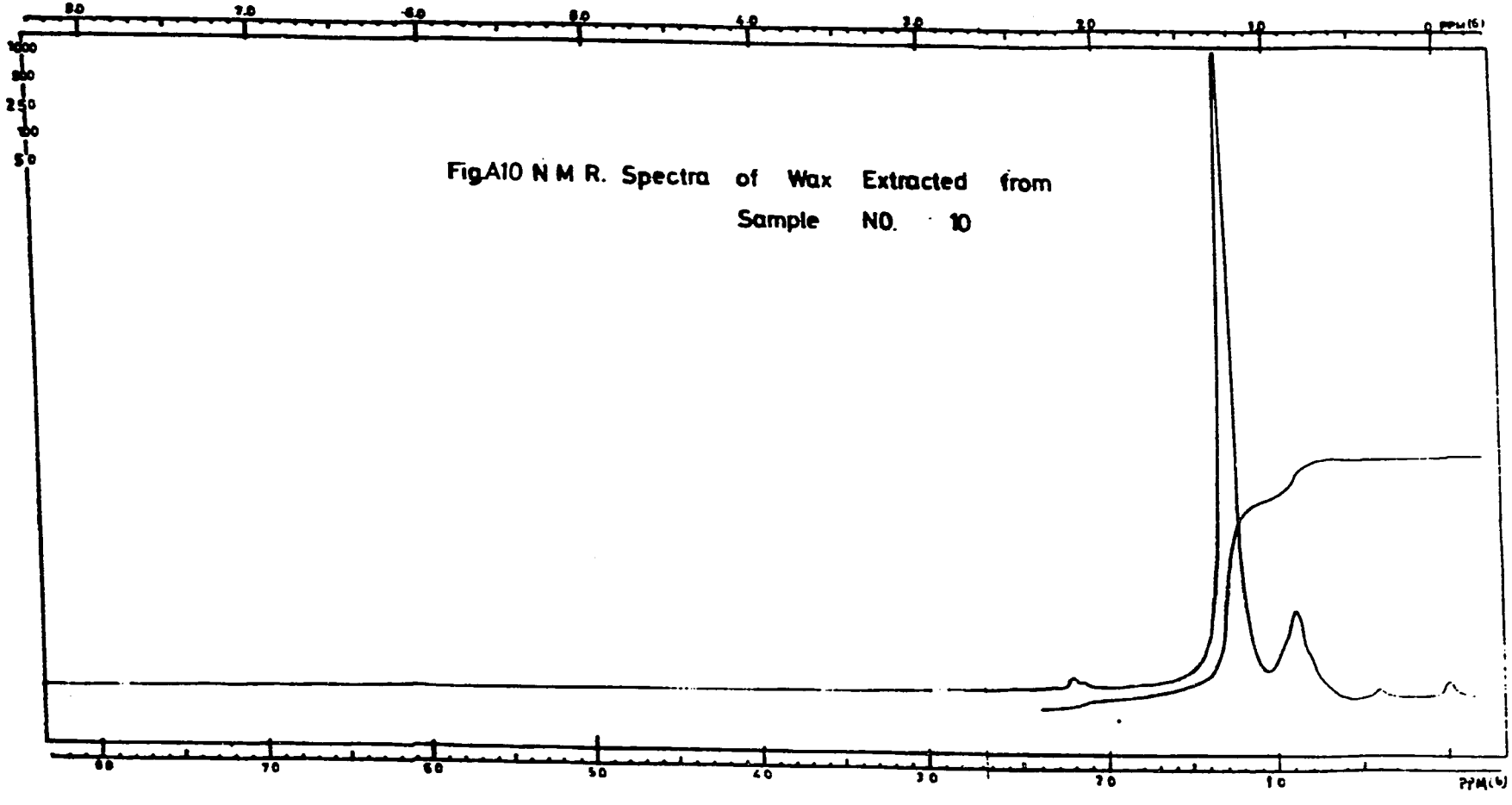

Fig.A10 N M R. Spectra of Wax Extracted from Sample NO. 10

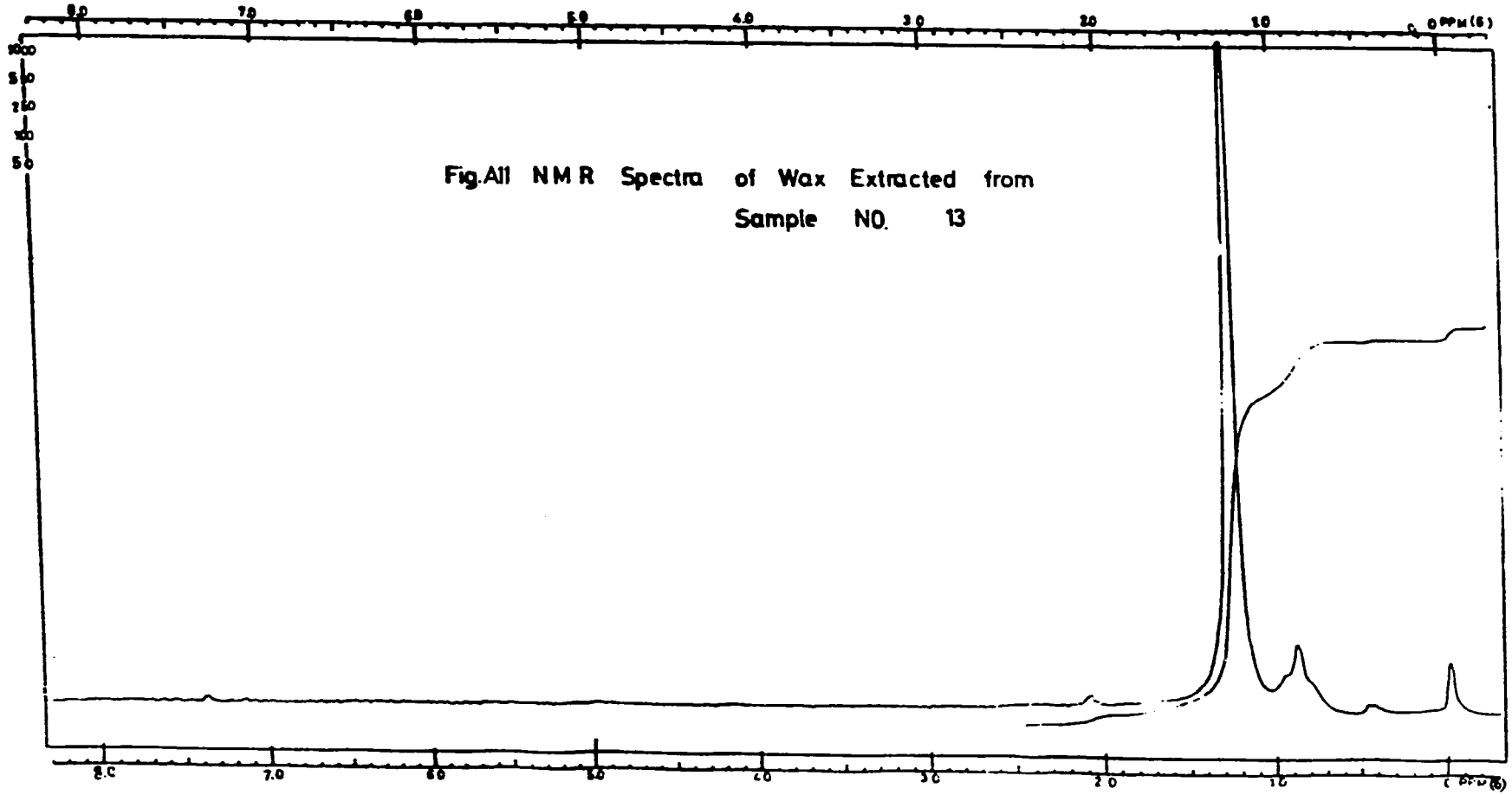

Fig.A11 NMR Spectra of Wax Extracted from Sample NO. 13

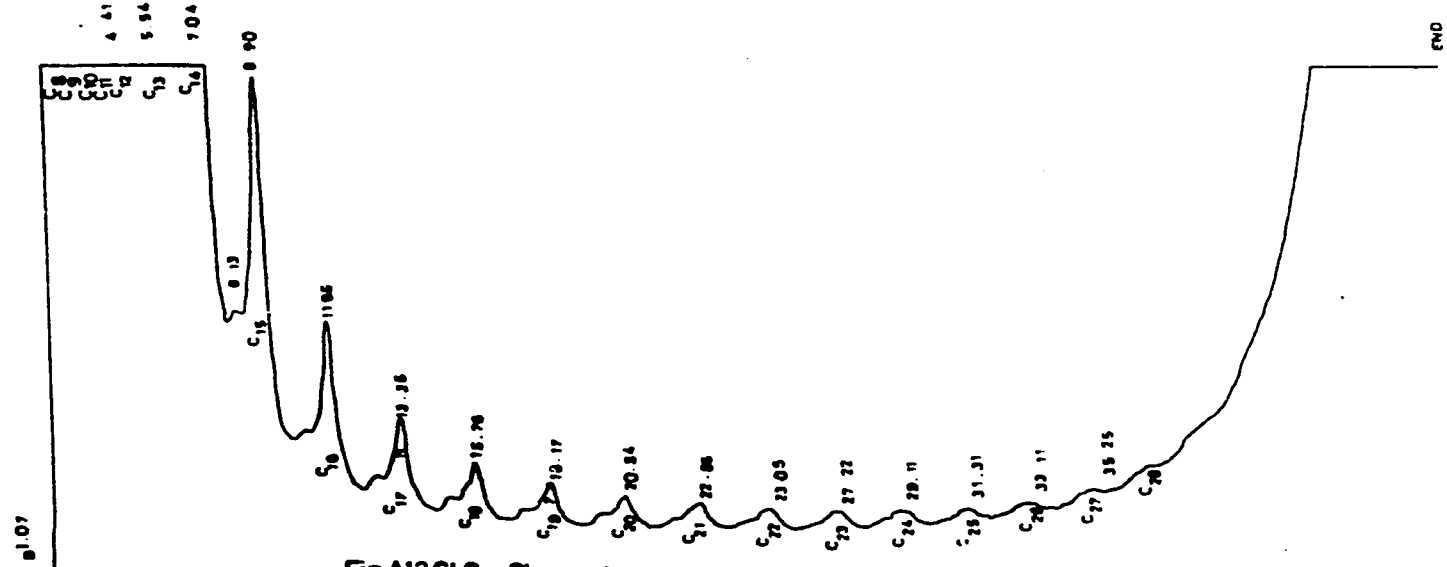

Fig.A12 GLC Chromatograms of the Wax Extracted from Sample No 1.

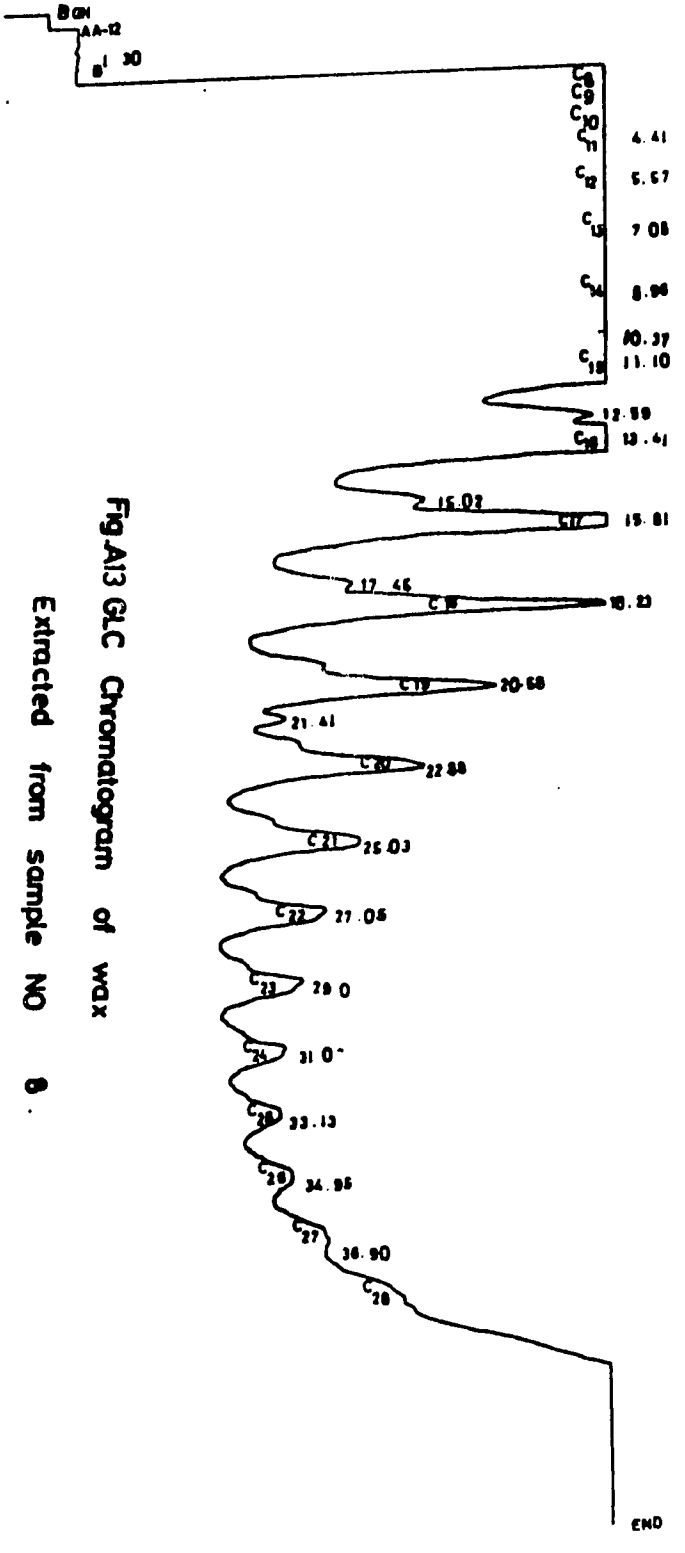

Fig.A13 GLC Chromatogram of wax

Extracted from sample NO 8.