TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
FHWA/TX-81/39+253-2		

4. Title and Subtitle	5. Report Date
AN EVALUATION OF THE ASPHALTENE SETTLING TEST	December 1981
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Thomas W. Kennedy and Chee-Chong Lin	Research Report 253-2

9. Performing Organization Name and Address	10. Work Unit No.
Center for Transportation Research The University of Texas at Austin Austin, Texas 78712	11. Contract or Grant No. Research Study 3-9-79-253
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address Texas State Department of Highways and Public Transportation; Transportation Planning Division P. O. Box 5051 Austin, Texas 78763	Interim
	14. Sponsoring Agency Code

15. Supplementary Notes

Study conducted in cooperation with the U. S. Department of Transportation, Federal Highway Administration

Research Study Title: "Moisture Effects on Asphalt Mixtures"

16. Abstract

This report describes a study which was undertaken to evaluate the asphaltene settling test, to investigate the possible relationships between settling time and physical properties of asphalt, and to determine the effect of asphalt modifiers and additives.

Two hundred and sixty-two virgin asphalt cements, 5 samples of extracted asphalts, 14 different anti-stripping agents, and 5 different asphalt softening agents were included in this study. Results of this study, along with previous findings at the Laramie Energy Technology Center, indicate that a great deal of additional work is required if the test is to have practical value and significance. Nevertheless the findings of this study indicate that the test has fair repeatability but is sensitive to test temperature. Settling times were very dependent on the producer; however, no relationships were found between test results and specification type asphalt characteristics. The addition of anti-stripping and softening agents tended to reduce settling times with respect to virgin asphalts.

A modified test procedure is recommended in order to simplify the procedure, to reduce time and cost of performing the test, and to improve the repeatability of the test.

17. Key Words	18. Distribution Statement
viscosity, asphaltene settling time, extracted asphalt, asphaltene dispersant, hexane-maltene phase, laboratory asphalt aging, asphalt modifiers, anti-stripping agent, asphalt softening agent, penetration	No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	71	

Form DOT F 1700.7 (8-69)

AN EVALUATION OF THE ASPHALTENE SETTLING TEST

by

Thomas W. Kennedy
Chee-Chong Lin

Research Report Number 253-2

Moisture Effects on Asphalt Mixtures
Research Project 3-9-79-253

conducted for

Texas
State Department of Highways and Public Transportation

in cooperation with the
U. S. Department of Transportation
Federal Highway Administration

by the

Center for Transportation Research
Bureau of Engineering Research
The University of Texas at Austin

December 1981

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 Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

PREFACE

This is the second in a series of reports dealing with the findings of a research project concerned with moisture effects on asphalt mixtures. This report summarizes the results of a limited study to

(1) evaluate the settling test in terms of test repeatability and the effect of variations in selected test variables on test results,

(2) utilize results from the settling test to evaluate the possible relationship between settling time and asphalt characteristics for asphalts from several producers, and

(3) use results from the settling test to evaluate the effectiveness of asphalt modifiers as asphaltene dispersants.

This report was completed with the assistance of many people. Special appreciation is extended to Messrs. James N. Anagnos, Pat Hardeman, and Eugene Betts for their assistance in the testing program and to personnel from the Texas State Department of Highways and Public Transportation who provided the asphalt cements and their physical properties. Appreciation is also extended to personnel from District 15 who assisted in obtaining the extracted asphalts used on the project and to the Center for Transportation Research staff who assisted in the preparation of the manuscript. The support of the Federal Highway Administration, Department of Transportation, is acknowledged.

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December 1981

LIST OF REPORTS

Report No. 253-1, "Stripping and Moisture Damage in Asphalt Mixtures," by Robert B. McGennis, Randy B. Machemehl, and Thomas W. Kennedy, summarizes a study to determine the extent, nature, and severity of moisture related damage to asphalt mixtures used in pavements in Texas.

Report No. 253-2, "An Evaluation of the Asphaltene Settling Test," by Thomas W. Kennedy and Chee-Chong Lin, summarizes a testing program designed to evaluate the asphaltene settling test, the procedures, and the factors affecting the test results and investigate possible relationships between settling time and asphalt characteristics.

ABSTRACT

This report describes a study which was undertaken to evaluate the asphaltene settling test, to investigate the possible relationships between settling time and physical properties of asphalt, and to determine the effect of asphalt modifiers and additives.

Two hundred and sixty two virgin asphalt cements, 5 samples of extracted asphalts, 14 different anti-stripping agents, and 5 different asphalt softening agents were included in this study. Results of this study, along with previous findings at the Laramie Energy Technology Center, indicate that a great deal of additional work is required if the test is to have practical value and significance. Nevertheless, the findings of this study indicate that the test has fair repeatability but is sensitive to test temperature. Settling times were very dependent on the producer; however, no relationships were found between test results and asphalt characteristics used in specifications. The addition of anti-stripping and softening agents tended to reduce settling times with respect to virgin asphalts.

A modified test procedure is recommended in order to simplify the procedure, to reduce time and cost of performing the test, and to improve the repeatability of the test.

KEY WORDS: asphaltene settling time, extracted asphalt, asphaltene dispersant, hexane-maltene phase, laboratory asphalt aging, asphalt modifiers, anti-stripping agent, asphalt softening agent, penetration, viscosity.

SUMMARY

The asphaltene settling test was designed to measure the compatibility of the components of an asphalt cement by measuring the settling rate of the asphaltenes for a mixture of asphalt and hexane. The results are reported as the length of time required for the asphaltenes to settle out of a solution of hexane. The primary premise upon which the settling test is based is that the mixtures with longer settling times are better dispersed in the hexane-maltene phase and that longer settling times indicate that the mixtures have more compatible components.

The purposes of this study were (1) to evaluate the settling test in terms of test repeatability and the effect of varying selected elements of the procedure on test results, (2) to determine the settling time of a series of asphalt cement specimens in order to investigate potential relationships between settling time and asphalt characteristics, and (3) to evaluate the effect of asphalt modifiers and softening and anti-stripping agents.

Based on the results of this study and previous experience at the Laramie Energy Technology Center, it is felt that a great deal of additional work is required if the test is to have a practical value. Nevertheless, the findings of this study indicate that

(1) the test has a fair repeatability, with coefficients of variation of settling times for 262 asphalts ranging from 2.8 to 9.4 percent;

(2) the settling time of asphalt is sensitive to the test temperature;

(3) the relationship between settling time and specification type asphalt characteristics (penetration, viscosity, specific gravity, flash point) was not well defined;

(4) the major factor that affected test results was the asphalt producer;

(5) the addition of anti-stripping agents reduced the settling time of virgin asphalts; and

(6) the effect on settling time of adding softening agents to virgin asphalt, artificially aged asphalt, and extracted asphalts was inconsistent.

A modified test procedure is included in the report. This modification was recommended in order to simplify the procedure, to reduce the time and cost of performing the test, and to improve the repeatability of the test.

IMPLEMENTATION STATEMENT

Based on the findings of the asphaltene settling time test, it is felt that additional consideration and evaluation must be given to this test before it can be used as a rapid way to determine the effectiveness of asphalt softening agents in asphalt mixtures. Additional study is needed to evaluate the potential relationships between settling time and performance characteristics of asphalt mixtures. Nevertheless, the results of a limited amount of testing indicated that the test has a fair repeatability and is sensitive to the test temperature. A slightly modified test procedure, based on the results of this study, is included in this report. This modification was recommended in order to simplify the procedure, to reduce the time and cost of performing the test, and to improve the repeatability of the test.

TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION

The objective of the study summarized in this report was to evaluate the asphaltene settling test (AST) which the Laramie Energy Technology Center (LETC) has suggested as a way to rapidly evaluate asphalt durability and the compatibility of asphalts and to determine how effective asphalt softening agents, which have been proposed for use in recycled asphalt mixtures, are in redistributing the molecular agglomerates present in aged asphalts.

The test is based on previous work (Refs 1 and 2), describing relationships between asphaltenes and durability, that, according to Plancher (Ref 3), led to the development of the settling test by Hoiberg and Suhaka for the Asphalt Roofing Manufacturers Association. Later modifications by Plancher made the test usable for paving grade asphalts (Ref 4). The test measures the relative degree of dispersion of asphaltenes of paving asphalts when the asphalts are dissolved in hexane. The dispersion is considered to represent a measure of the compatibility of the asphalt components, which is important to asphalt chemistry (Ref 3). Test results are reported as a settling time or settling rate of the asphaltene in the solution of asphalt and hexane.

Because of the work related to the use of this test by Plancher, Petersen, and others at the Laramie Energy Technology Center, various agencies and groups have begun to use the test or to consider it for use. Plancher et al (Ref 3) reported several advantages to this test: (1) good repeatability and high sensitivity to changes in asphalt composition and (2) applicability to virgin, recovered or aged, modified, and blended asphalts. Modified asphalts are asphalts which have been mixed with modifiers, such as asphalt softening, or rejuvenating agents.

Even though LETC has done a considerable amount of development work with the test, it has not otherwise been used extensively nor been applied to a large number of asphalts. The primary objective of the study summarized in

this report is to evaluate the asphaltene settling test and determine the factors which affect it. Chapter 2 includes a description of the test, theory, and experimental program. Chapter 3 contains the analysis and findings of the study. Chapter 4 includes the conclusions and recommendations.

CHAPTER 2. TEST DESCRIPTION AND EXPERIMENTAL PROGRAM

According to Plancher et al (Ref 3) asphalt has traditionally been considered to be composed of oils, asphaltenes, and resins but it is more correctly a mixture of complex molecular structures ranging from paraffinic types to highly condensed ring structures with varying degrees of aromaticity, substitution, and heteroatom content. They have also suggested that asphalt compatibility is related to the interaction of molecular components and that changes in the asphalt components could affect the compatibility of the asphalt mixture which, in turn, could affect its performance characteristics. Some of the factors which could affect component compatibility are original composition, feedstock blending, aging, asphalt modifiers, and the adsorption characteristics of the mineral aggregates.

The asphaltene settling test was developed to measure the compatibility of the components of an asphalt cement by measuring the asphaltene settling rate for a mixture of asphalt and hexane. Typical settling rate relationships are shown in Fig 1. Because many of the relationships related to particles settling from a solution were linear over a reasonable period of time, the time required for the asphaltenes to settle to the 25-ml level in a graduated cylinder was adopted by LETC as the settling time. The slower the settling rate, or the longer the settling time, the more compatible the asphalt components. This measure of compatibility is based on the premise that asphaltenes with longer settling times are better dispersed in the hexane-maltene phase than those with shorter settling times (Ref 3). Plancher also noted that the test results could be affected by the quantity, size, shape, and density of the asphaltene particles and by the viscosity and density of the hexane-maltene phase. Likewise, the effect of changes in test variables, such as quantity of asphalt, test temperature, etc., has not been systematically studied to any extent.

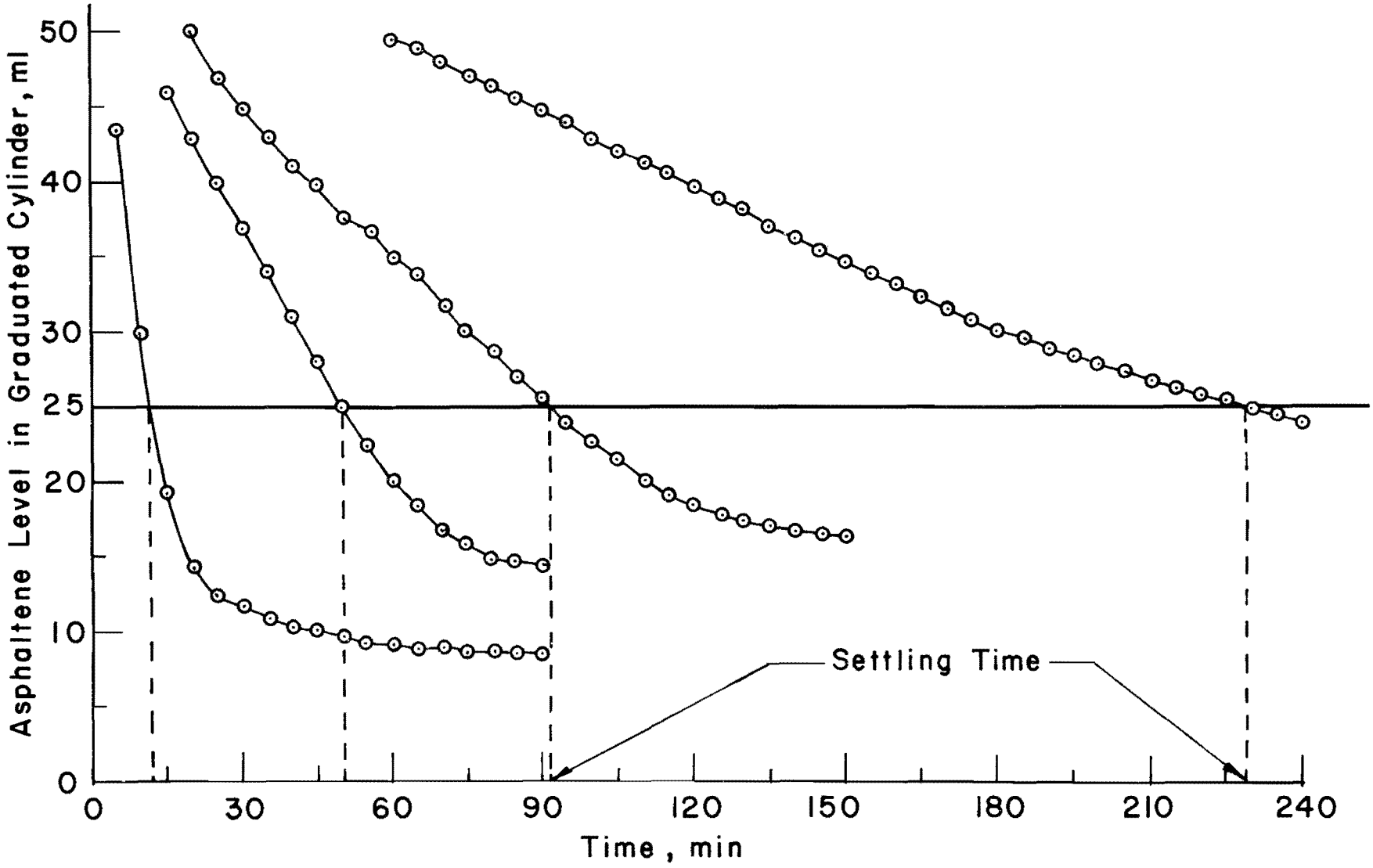

Fig 1. Typical asphaltene settling curves.

Aged asphalts generally have longer settling times than virgin asphalts. This increase in settling time is partially attributed to increased viscosity of the hexane-maltene solution, charged particles, changes in asphaltene geometry with increased aging levels (spherical to platelets), density, etc.; therefore, it should not be construed that aged asphalts are more compatible or durable simply because they have longer settling times. Caution should be exercised when comparing asphalt systems (Ref 4).

OBJECTIVES

This study was developed to evaluate the asphaltene settling test. This evaluation included determining

(1) the repeatability for
   (a) tests conducted simultaneously by the same operator or at the same time by two different operators,
   (b) tests conducted over a period of time by the same operator,
   (c) tests conducted by different laboratories*; and
(2) the effect of variations of the following variables on test results
   (a) amount of asphalt,
   (b) asphalt preparation temperature, and
   (c) test temperature.

An additional objective was to use the test to investigate

(1) the relationship between the asphaltene settling time and asphalt characteristics for various producers and
(2) the effect of commonly used additives or modifiers, such as anti-stripping agents and asphalt softening agents, on test results.

*Asphalt cements had been sent to LETC, but the results were not available at the time of this report.

TEST METHOD

The asphaltene settling test proposed by the LETC involves the following steps.

(1) Dissolve 2.0000 grams of asphalt cement in 50 ml of n-hexane by stirring the mixture for 16 to 24 hours at 20°C (68°F),*
(2) Transfer the digested mixture into a 50-ml graduated cylinder,
(3) Read the asphaltene level in the graduated cylinder at 5-minute intervals and record.

The asphalt settling time is defined as the time, in minutes, required for the asphaltene meniscus to descend to the 25-ml level in the 50-ml graduated cylinder (Ref 3). Additional details of the test and required equipment are contained in Appendix A.

MATERIALS

Materials included in the study were virgin asphalt cements, extracted asphalts, anti-stripping agents, and asphalt softening agents. The anti-stripping and softening agents were included in order to determine the effects of these additives on the settling times.

Except for the extracted asphalts, the asphalt cements were identified using an alpha numeric code in which a letter represented the producer and a number represented a sample of asphalt from that producer. For anti-stripping agents, the producer identification letter was preceded by an A, and for softening agents it was preceded by an R. The extracted asphalts were identified with an EE. These asphalts were extracted in 1980 and the solvent used in the extraction was trichloroethylene.

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*A stirring time of 20 hours was used in this and subsequent studies.

Asphalt Cements

Tests were performed on 262 virgin asphalts and 5 samples of an extracted asphalt that were obtained from the Texas State Department of Highways and Public Transportation (DHT). Virgin asphalts were secured from 16 different producers in Texas and Oklahoma and included grades ranging from AC-3 to AC-20.

Asphalt Modifiers

The two categories of additives, or modifiers, used were anti-stripping agents and asphalt softening agents. Fourteen types of anti-stripping agents provided by seven producers and five types of asphalt softening agents provided by five producers were included in the test program.

EXPERIMENTAL PROGRAM

Tests were conducted to evaluate the (1) test repeatability, (2) effect of test variables, (3) relationship of settling time to asphalt characteristics, and (4) effects of asphalt modifiers on settling times.

Repeatability

To evaluate the repeatability of the test, two test programs were conducted: in one program tests were conducted simultaneously by (a) the same operator or (b) different operators, and in the other tests were conducted over a period of time by the same operator.

Because of the limited amount of extracted asphalt cement available, only virgin asphalt cements were utilized in this portion of the study. The selected asphalt cements covered a viscosity range from AC-3 to AC-20 and provided a wide range of settling times. Ten tests on each of seven asphalt

cements, representing five producers, were conducted simultaneously by one operator. In addition, a second operator conducted a similar series of ten tests on each of five of the above asphalt cements. To evaluate time effects, eight asphalt cements from six producers were tested ten times over a ten-day period. Table B.1 summarizes the test program.

Test Variables

As discussed below, the test variables selected for study were (1) amount of asphalt, (2) asphalt preparation temperature, and (3) test temperature.

Amount of Asphalt. The original test method specified 2.0000 grams of asphalt cement. The time and care required to measure such a precise quantity of asphalt cement adds significantly to the cost and difficulty of performing routine multiple tests. Thus, tests were conducted to determine the effect on test results by varying the amount of asphalt cement. Four asphalt cements from four different producers and with viscosity grades of AC-10 and AC-20 were selected for testing. Three replicate specimens were prepared at 1.9000, 1.9900, 2.0000, 2.0100, and 2.1000 grams for each asphalt cement.

Asphalt Preparation Temperatures. Since heating greatly facilitates obtaining a precise amount of asphalt, it was desirable to determine if heating the asphalt cement in sealed containers had an effect on test results. Thus, tests were conducted to evaluate the effect oof cyclically heating the asphalt cement from room temperature, 24°C (75°F), to 82°C (180°F). For two asphalt cements one specimen was tested after each reheating, up to ten times, and 20 asphalt cements were heated one time and one specimen was tested.

Test Temperature. Two temperatures were selected for conducting the asphaltene settling test, 20°C (68°F) and 24°C (75°F), i.e., room temperature. Although 20°C (68°F) was proposed by LETC, room temperature would be much more convenient. Thus, duplicate specimens were tested in

order to evaluate the effect of testing at temperatures of 20°C (68°F) and 24°C (75°F) on settling test results. Ten asphalts from four producers with a viscosity range from AC-3 to AC-20 were tested.

Relationship to Asphalt Characteristics

Two hundred and sixty two virgin asphalt cements were tested to determine the resulting asphaltene settling times. Samples of these asphalt cements were secured from 16 producers in Texas and Oklahoma and represent grades ranging from AC-3 to AC-20, as shown in Table B.2. Possible relationships were investigated between settling time and the asphalt cement specification properties determined and supplied by the Texas Department of Highways and Public Transportation (DHT).

Effects of Asphalt Modifiers

The two categories of modifiers tested were anti-stripping agents and asphalt softening agents.

Anti-stripping Agents. Tests were conducted on mixtures containing virgin asphalts plus various anti-stripping agents to evaluate the effect produced by the addition of the anti-stripping agent. Each of three asphalt cements was tested with fourteen different anti-stripping agents. The amount of the anti-stripping agents was 10 percent of the weight of the asphalt cement.

Asphalt Softening Agents. Two series of tests were performed to determine the effect of asphalt softening agents on the settling times of virgin, artificially aged, and extracted asphalts. In one series, settling times were determined for artificially aged asphalts to which three different asphalt softening agents were added, as shown in Table B.3. The aging was accomplished by heating the asphalt cement to 121°C (250°F) for specified periods of time. The two quantities of asphalt softening agents used in these tests were one and 15 percent of the weight of the asphalt cement.

In the second series, one settling time was determined using each of five samples of an extracted asphalt. Additional specimens were prepared with each of four asphalt softening agents added to the extracted asphalt. The amount of softening agent was 15 percent of the weight of the extracted asphalt.

CHAPTER 3. ANALYSIS AND DISCUSSION OF TEST RESULTS

The primary objectives were to determine the repeatability of the test, the effects and importance of modifying various test parameters on test results, the relationship between asphaltene settling time and asphalt cement characteristics, and the effect of commonly used modifiers on the settling times of virgin asphalt.

REPEATABILITY TESTS

Two types of repeatability tests were conducted: (1) repeatability of simultaneous tests by the same operator or different operators and (2) repeatability of tests over a period of time by the same operator. Approximately ten settling tests were conducted simultaneously by one operator on seven asphalts and by a second operator on five asphalts. In addition, ten replicated tests on eight asphalts were conducted over a period of ten days by one operator. The resulting settling times are summarized in Tables 1 and 2 and in Figs 2 and 3.

As can be seen, the range for the settling times obtained for the various test series varied from 2.4 to 14.0 minutes for operator 1 and from 4.1 to 17.5 minutes for operator 2. The corresponding values of the standard deviation were 0.84 to 4.24 for operator 1 and 1.31 to 5.31 for operator 2. Since the mean settling times varied significantly for the various test series, coefficients of variation were calculated. These coefficients varied from 2.8 to 9.2 percent for operator 1 and from 4.9 to 9.4 for operator 2. Thus, the repeatability was fair and it would appear to be essentially the same for the two operators.

A comparison of the mean values, however, indicates that operator 2 generally obtained shorter settling times. This variation probably is significant statistically; however, it is not of practical

TABLE 1. SUMMARY OF REPEATABILITY OF ASPHALTENE SETTLING TEST FOR SIMULTANEOUS TESTS

Producer and Specimen Number	Operator	Asphaltene Settling Time, min										Extremes, min	Range, min	Mean, min	Std. Dev., min	Coefficient of Variation, %
		Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10					
A9	1	30.0	28.2	30.0	29.6	28.7	29.3	28.1	29.0	27.6	28.2	27.6-30.0	2.4	28.9	0.84	3.0
	2	30.6	28.7	30.7	31.0	26.6	28.6	-	27.5	-	27.9	26.6-31.0	4.4	28.9	1.64	5.7
B15	1	33.5	34.3	30.4	30.5	29.2	33.9	34.8	34.2	36.4	35.6	29.2-36.4	7.2	33.3	2.41	7.2
	2	32.4	31.2	31.2	31.2	29.1	31.4	26.3	31.5	33.7	30.5	26.3-33.7	7.4	30.9	1.99	6.4
C20	1	32.7	31.1	28.8	28.0	26.6	27.8	23.6	30.0	31.2	30.9	23.6-32.7	9.1	29.1	2.69	9.2
	2	26.5	29.2	27.2	27.0	25.5	25.5	24.9	28.0	25.8	26.0	24.9-29.0	4.1	26.6	1.31	4.9
D4	1	59.0	62.6	53.8	53.7	57.6	51.0	57.6	60.0	65.0	59.0	51.0-65.0	14.1	57.9	4.24	7.3
	2	53.9	65.0	53.0	49.0	49.0	55.2	-	52.7	55.4	58.0	49.0-65.0	16.0	54.6	4.87	8.9
D5	1	60.0	62.6	57.6	59.5	62.2	62.6	54.0	62.6	62.5	62.2	54.0-62.6	8.6	60.6	2.88	4.8
	2	60.6	57.7	54.0	45.0	55.0	56.0	-	56.7	62.5	62.0	45.0-62.5	17.5	56.6	5.31	9.4
A249	1	24.1	21.7	22.5	22.5	22.2	21.1	22.0	21.1	-	-	21.1-24.1	3.0	22.2	0.96	4.3
H245	1	98.5	98.4	104.1	104.1	97.5	104.1	102.7	102.0	98.2	-	98.2-104.1	5.9	101.1	2.87	2.8

Test temperature = 20°C (68°F)

TABLE 2. SUMMARY OF REPEATABILITY OF ASPHALTENE SETTLING TEST FOR DAILY RUNS

Producer and Specimen Number	Asphaltene Settling Time, min										Extremes, min	Range, min	Mean, min	Std. Dev., min	Coefficient of Variation, %
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10					
A9	28.8	28.7	31.5	29.4	29.4	28.6	29.1	29.4	29.9	30.4	28.6-31.5	2.9	29.5	0.89	3.0
A53	23.6	24.9	25.0	25.0	24.1	22.2	22.8	22.8	23.7	23.1	22.2-25.0	2.8	23.7	1.01	4.3
B15	30.0	30.0	32.6	34.8	33.3	31.3	30.9	31.5	34.0	30.7	30.0-34.8	4.8	31.9	1.68	5.3
C20	30.5	27.3	28.4	29.0	28.9	28.7	32.5	28.0	27.1	28.0	27.1-32.5	5.4	28.8	1.61	5.6
D4	59.7	56.3	58.4	61.8	69.0	57.3	62.0	60.0	58.9	62.3	56.3-69.0	12.7	60.6	3.58	6.9
D5	60.5	60.2	66.2	60.0	58.0	62.2	59.5	61.4	63.2	57.3	57.3-66.2	8.9	60.9	2.58	4.2
G178	73.5	78.0	75.0	79.6	69.7	72.5	71.4	72.7	77.2	77.5	69.7-79.6	9.9	74.7	3.25	4.4
P170	126.3	130.4	126.9	121.8	127.7	125.0	130.0	131.0	125.5	133.6	121.8-133.6	11.8	127.8	3.46	2.7

Test temperatures = 20°C (68°F)

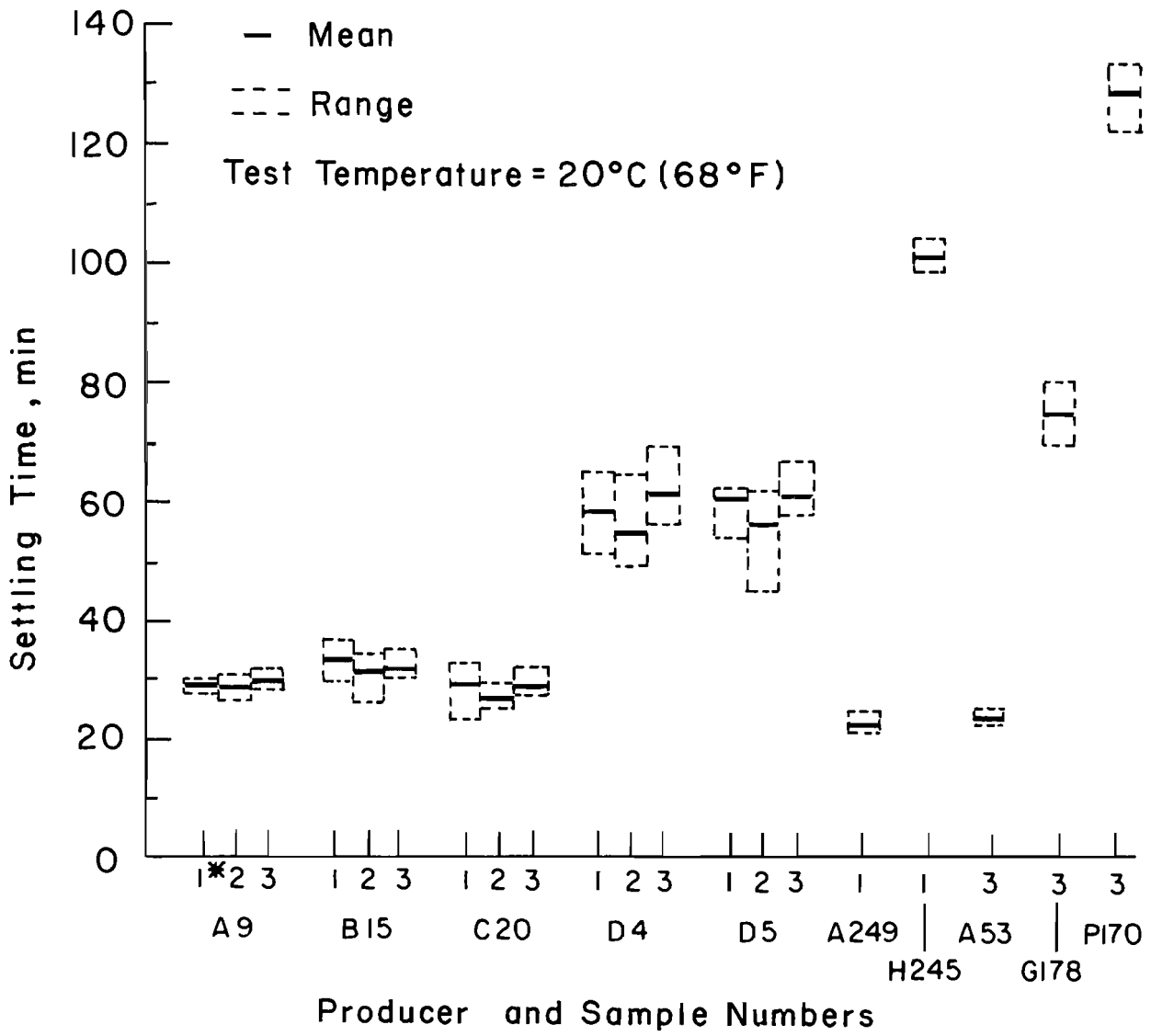

Fig 2. Repeatability of asphaltene settling test for different operators and time periods.

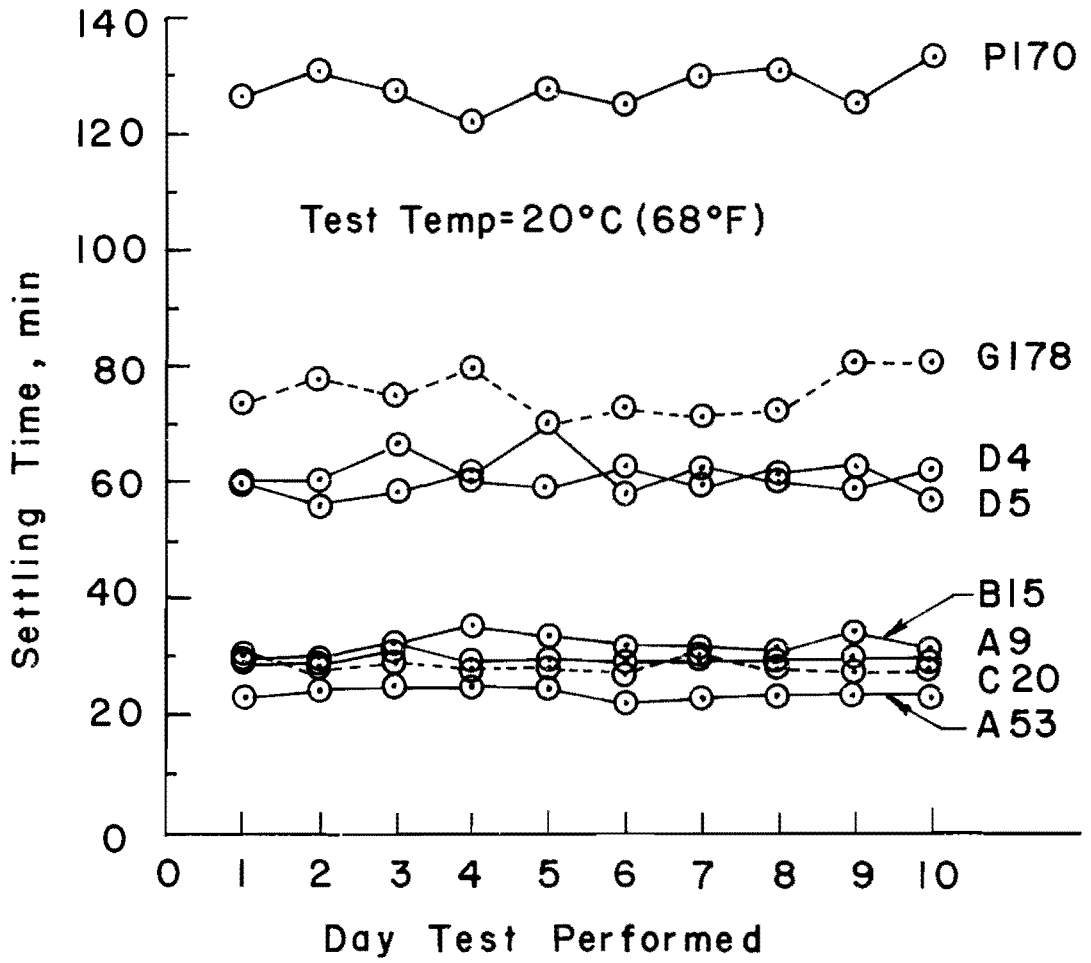

Fig 3. Repeatability of asphaltene settling test conducted over a period of time.

significance since the range of values for any given test series was much larger than the difference between operators. This difference could be attributed to sampling techniques, temperature control, or rate of digestion, i.e., stirring rate. However, due to the consistencies of the differences, it is felt that the more probable cause is the time required to transfer the solution to the graduated cylinder at the beginning of the timing process. It is, therefore, recommended that the timing of the test start 20 seconds after stirring ends.

In addition, consideration should be given to eliminating the 10 ml hexane wash since it is felt that the amount of residue left in the flask probably would not affect the test results but that the change in mixture concentration in the upper portion of the cylinder could quite easily affect test results. The washing process definitely adds to the time required for transfer and in fact is responsible for the largest portion of the transfer time.

The settling times obtained from the series of tests conducted over a period of time are summarized in Table 2 and Fig 3. The relationships shown in Fig 3 do not indicate any consistent changes with time. The range and standard deviations varied from 2.8 to 12.7 and from 0.89 to 3.58, respectively. The coefficients of variation varied from 2.7 to 5.9 percent, which are consistent with the values obtained by simultaneous multiple tests conducted by the same operator. These results suggest that well trained operators can probably repeat the test over a period of time as well as they can repeat it at any given time.

Samples of the asphalt were sent to the Laramie Energy Technology Center in order to develop between-laboratory comparisons; however, their results were not available at the time of this report.

TEST VARIABLES

Three test variables, two associated with mixture preparation and the other with testing temperature, were evaluated to determine the effect of changes in each variable on test results.

Mixture Preparation

The amount of asphalt and the effect of heating the asphalt during weighing of the asphalt are important with respect to the time required for sample preparation. Thus, the effects of changes in these two variables were evaluated.

Amount of Asphalt. A series of tests on asphalts exhibiting mean settling times ranging from 23 to 98 minutes was conducted to determine the effects and importance of variations in the amount of asphalt on test results. Mixtures containing 1.9000, 1.9900, 2.0000, 2.0100, and 2.1000 grams of asphalt were prepared and tested. The resulting settling times are summarized in Table 3 and Fig 4.

No consistent relationship was found between the amount of asphalt used in the mixture and settling time. At or near 2.0000 grams there appears to be a significant hump in the relationship. This inconsistency is attributed to the short range over which these three test were plotted, which exaggerates the variation. In fact the magnitude of the effect is less than the range of values which could be expected with replicated tests (Tables 1 and 2). It, therefore, is apparent that the amount of asphalt is not particularly important. Thus, to facilitate sample preparation in production operations but at the same time to provide reasonable control, it is recommended that the asphalt be weighed to 2.00 grams with an accuracy of $\pm$ .01 grams.

Heating the Asphalt. Heating the asphalt to 82°C (180°F) to facilitate weighing the required amount of asphalt to be used in the partial solution of asphalt cement and hexane did not produce any consistent effect on the settling times nor did repeated heatings have an effect (Tables 4 and 5 and Figs 5 and 6). Erratic results were observed in the repeated heating tests on asphalt cement P299 (Fig 6) which could have been the result of many testing or sampling variations. Nevertheless, it is recommended that the asphalt cement not be heated prior to weighing since asphalt properties could be adversely affected.

TABLE 3. THE EFFECT AND IMPORTANCE OF THE AMOUNT OF ASPHALT USED IN THE MIXTURE ON SETTLING TIME

Producer and Specimen Number	Amount of Asphalt, g	Asphaltene Settling Time, min			
		Test 1	Test 2	Test 3	Mean
A139	1.9000	24.1	23.5	24.9	24.1
	1.9900	20.1	19.7	19.7	19.8
	2.0000	23.6	22.5	23.7	23.2
	2.0100	19.9	20.3	21.8	20.6
	2.1000	22.1	23.5	24.5	23.3
B76	1.9000	37.6	36.6	36.8	37.0
	1.9900	34.7	31.4	33.1	33.0
	2.0000	37.7	37.1	36.6	37.1
	2.0100	36.9	34.1	36.1	35.7
	2.1000	38.4	41.8	37.8	39.3
H245	1.9000	97.4	95.8	104.1	99.1
	1.9900	95.8	96.6	100.0	97.4
	2.0000	97.8	99.1	96.6	97.8
	2.0100	96.8	100.0	102.8	99.8
	2.1000	109.1	109.1	105.4	107.8
L181	1.9000	54.1	59.1	52.7	55.3
	1.9900	61.1	63.9	57.2	60.7
	2.0000	59.5	59.0	56.6	58.3
	2.0100	64.7	59.5	62.4	62.2
	2.1000	67.5	65.9	60.7	64.7

Test temperature = 20°C(68°F)

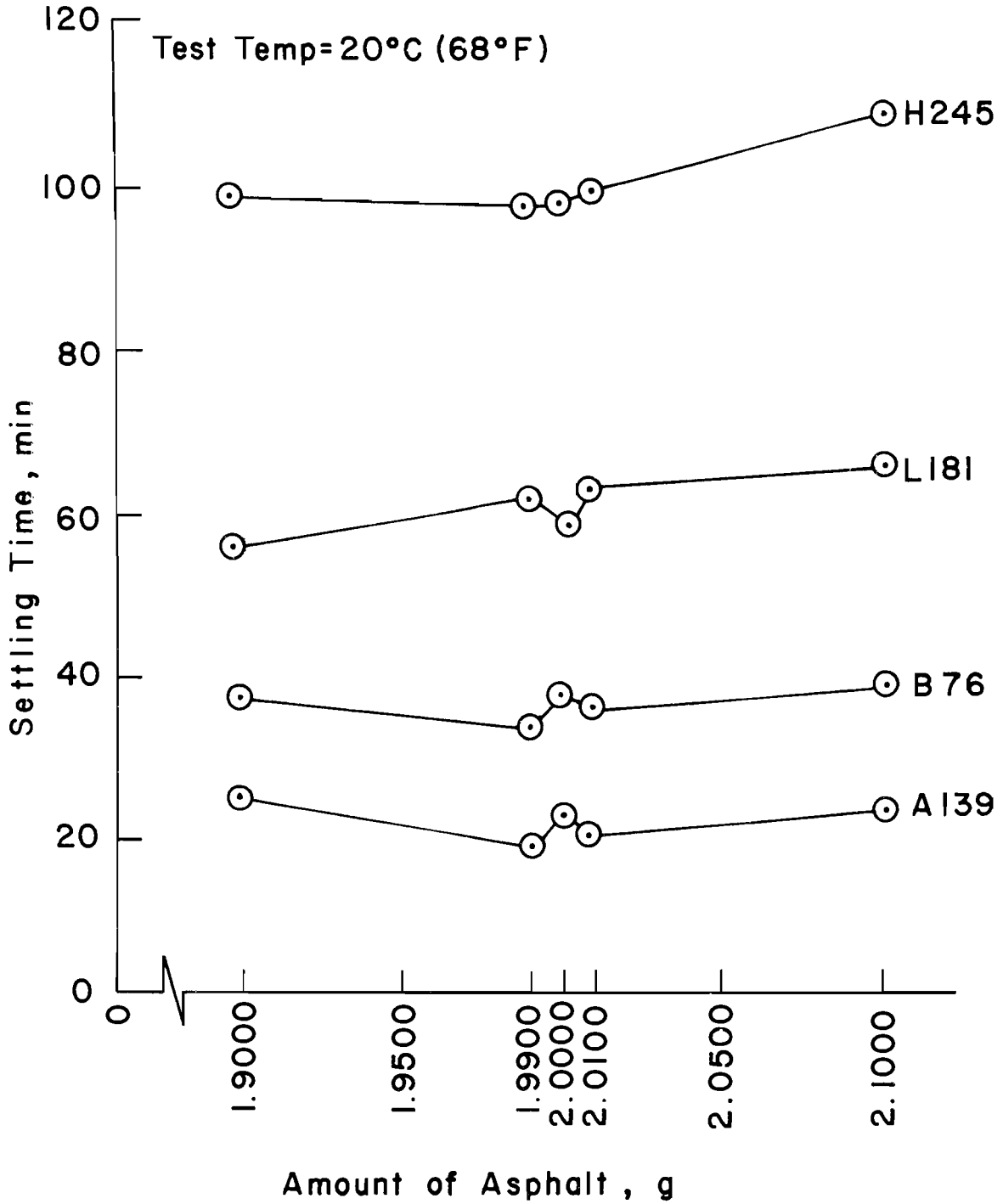

Fig 4. Relationships between amount of asphalt in the mixture and settling time.

TABLE 4. THE EFFECT ON SETTLING TIME OF HEATING THE ASPHALT DURING SAMPLE PREPARATION

Producer and Specimen Number	Asphaltene Settling Time, min			
Sample Prep. Cond.	Unheated			Heated
	Test 1	Test 2	Mean	
A53	23.6	24.9	24.2	24.5
A54	19.3	19.9	19.6	21.6
A55	24.1	26.8	25.4	25.0
A140	38.2	39.1	38.7	39.4
B75	35.0	33.6	34.3	33.7
B150	33.9	35.3	34.6	34.5
B151	32.1	31.3	31.7	35.0
B152	32.3	35.7	34.0	32.8
B153	36.4	35.7	36.0	36.6
B154	30.0	32.3	31.1	31.3
B155	30.7	31.8	31.2	32.9
G176	60.0	62.7	61.3	64.0
G177	57.7	56.9	57.3	65.2
G178	73.5	78.0	75.7	77.9
G186	15.7	16.2	15.9	16.0
G187	20.0	21.8	20.9	20.0
P169	150.0	146.5	148.3	145.0
P170	126.3	130.4	128.3	136.4
P171	135.0	130.4	132.7	142.7
P299	66.9	65.0	66.0	67.5

Unheated specimens were prepared at 24°C (75°F); heated, at 82°C (180°F).

Test temperature = 20°C (68°F)

TABLE 5. THE EFFECT ON SETTLING TIME OF REPEATED HEATING OF THE ASPHALT CEMENT DURING SAMPLE PREPARATION

Heating Cycles / Producer and Specimen No.	Asphaltene Settling Time, min										
	0	1	2	3	4	5	6	7	8	9	10
A54	19.6	21.6	23.4	21.3	22.0	23.5	24.1	24.3	22.0	23.5	22.6
P299	66.0	65.6	-	58.9	74.7	69.5	68.7	65.0	67.6	70.0	69.0

Sample was heated to 82°C(180°F)
Test temperature = 20°C(68°F)

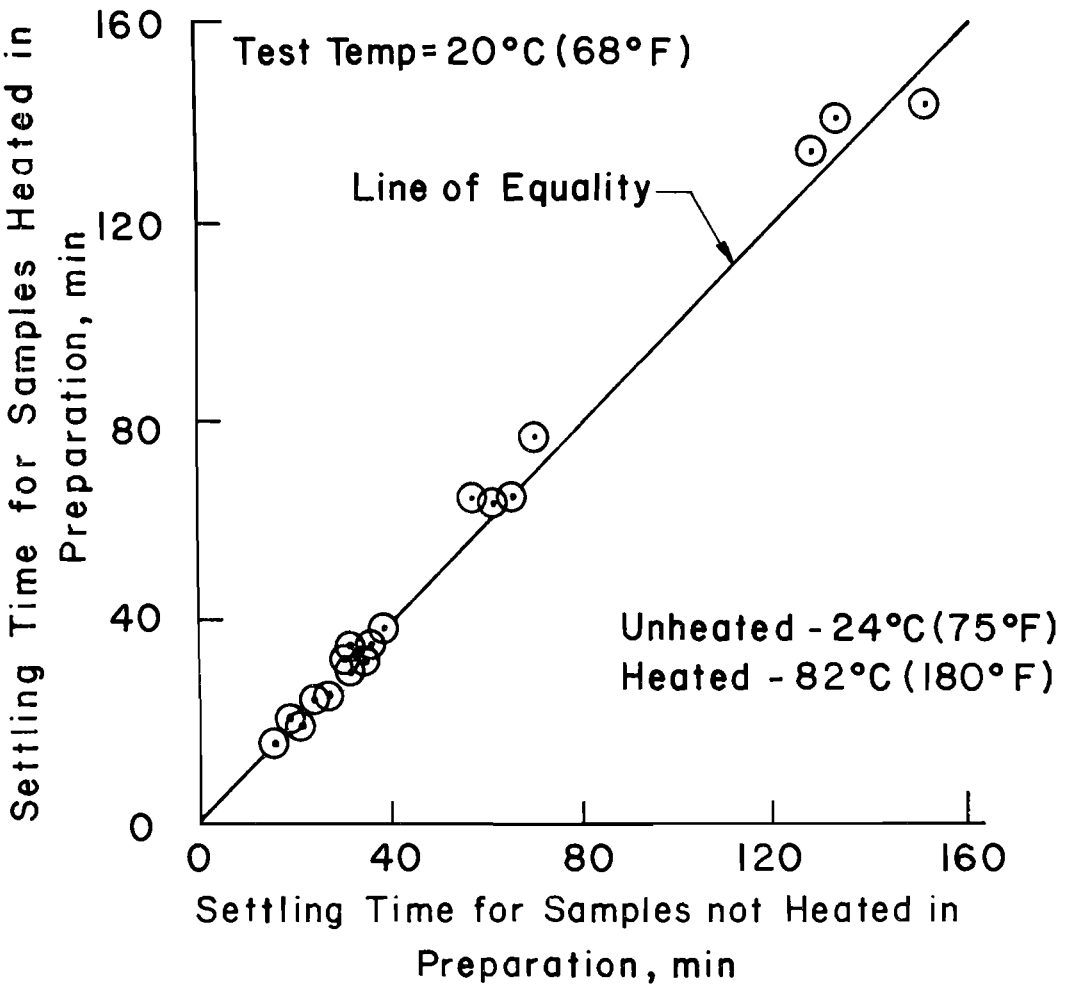

Fig 5. Effect on settling time produced by heating asphalt cement at time of weighing.

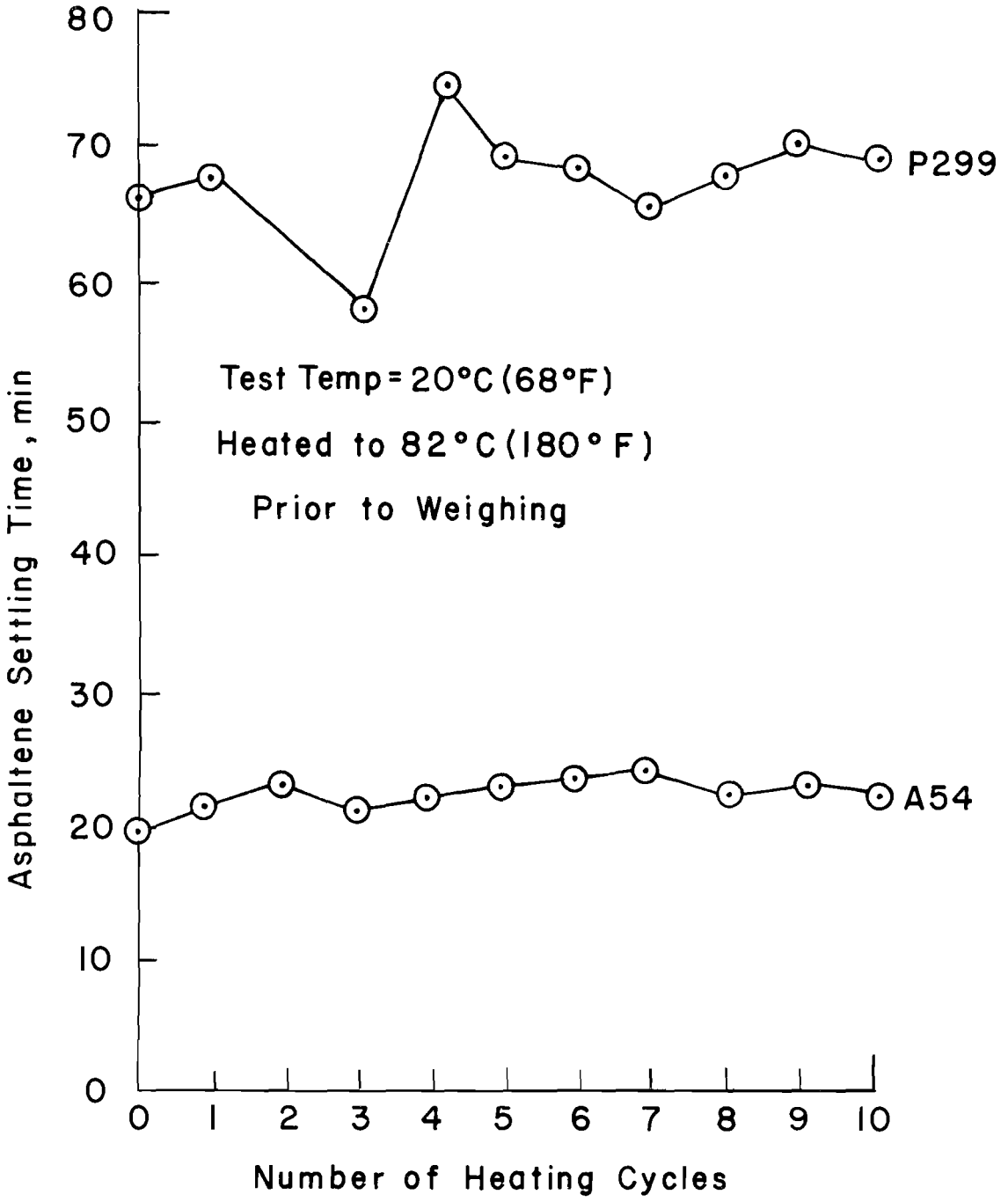

Fig 6. Relationship between settling time and the number of heating cycles prior to weighing the asphalt cement.

Test Temperature

Ten asphalts having a wide range of settling times were selected and tested at temperatures of 24°C (75°F) and 20°C (68°F). The resulting settling times are summarized in Table 6 and Fig 7. As shown in Fig 7, the asphaltene settling times at 20°C (68°F) were substantially higher than at 24°C (75°F), partially due to viscosity effects. The effect is large enough to require control of the test temperature. Water baths or controlled environment chambers are probably required and justified.

RELATIONSHIP TO ASPHALT CHARACTERISTICS

A limited analysis was conducted to investigate potential relationships between settling time and physical specification properties supplied by the DHT for 55 asphalt cements. Properties analyzed were viscosity, penetration, specific gravity, and flash point. Asphaltene settling times were determined for each virgin asphalt and the results compared to the physical properties of the asphalt cements contained in Table 7.

No relationships between asphaltene settling time and these physical properties of the asphalt cements were found to exist. This result was not unexpected since many of these properties are controlled during production and are only indirectly related to the properties of the asphalt, e.g., flash point. Examples of the nature of the relationships involving viscosity and penetration are shown in Figs 8 through 11. Settling times, however, are related to other rheological properties or characteristics (Ref 4). The Laramie Energy Technology Center has 33 of these asphalts for rheological testing and further evaluation. Results, however, were not available at the time of this reporting.

Asphalt Producers

The only factor found to affect settling time was asphalt producer, which probably is related to composition. Fig 12 and Table 8 summarize the mean and standard deviation of settling times for the 16 producers located in Texas and Oklahoma.

TABLE 6. THE EFFECT OF TEST TEMPERATURE ON SETTLING TIME

Producer and Specimen Number	Asphaltene Settling Time, min					
	Test 1		Test 2		Mean	
	24°C (75°F)	20°C (68°F)	24°C (75°F)	20°C (68°F)	24°C (75°F)	20°C (68°F)
A1	16.0	29.0	22.9	30.0	19.4	29.5
A8	25.0	28.0	24.1	31.0	24.5	29.5
A9	19.1	23.0	19.6	25.0	19.3	24.0
A10	18.3	22.0	19.1	24.1	18.7	23.0
B2	32.3	41.0	30.1	40.0	31.2	40.5
C3	48.1	61.0	50.8	54.0	49.4	57.5
D4	45.0	67.5	45.0	65.0	45.0	66.2
D5	53.2	69.0	46.0	66.0	49.6	67.5
D6	-	70.0	56.2	63.5	56.2	66.7
D7	42.6	59.0	38.3	57.5	40.4	58.2

Test Conditions:
Test temperature at 24°C(75°F) - 2.0000 g,
82°C(180°F) Preparation Temperature
Test temperature at 20°C(68°F) - 2.0000 g,
82°C(180°F) Preparation Temperature

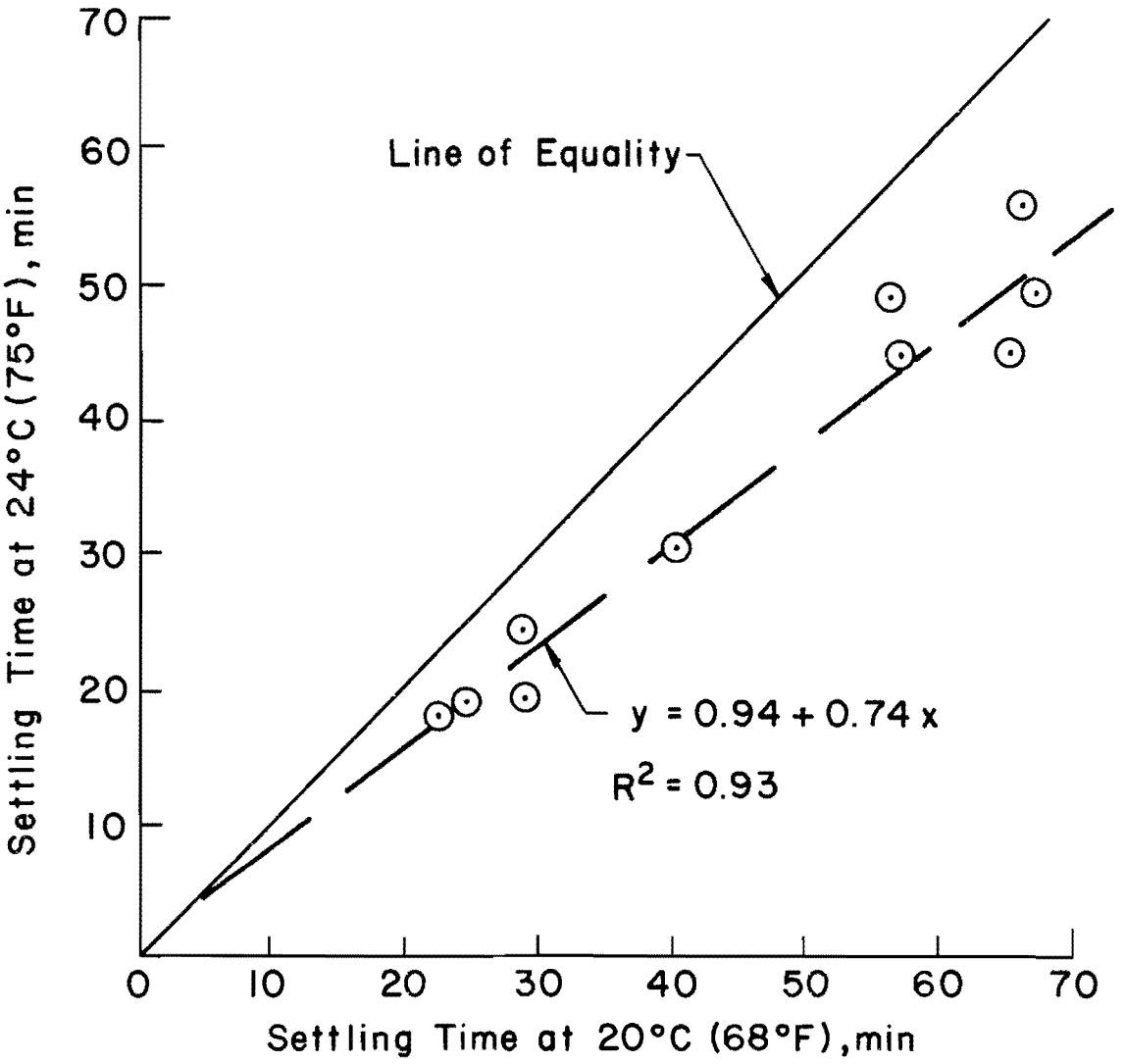

Fig 7. Effect of test temperature on settling time.

TABLE 7. ASPHALT CHARACTERISTIC TEST RESULTS FOR ASPHALT CEMENTS FROM VARIOUS PRODUCERS

Producer	Virgin Asphalt								Residue from TFO Test	
	Viscosity Grade	Settling Time, min	Viscosity at 60°C (140°F), Stokes	Viscosity at 135°C(275°F), Stokes	Penetration at 25°C (77°F)	Specific Gravity at 15.6°C(60°F)	Specific Gravity at 25°C(77°F)	Flash Point, °C	Viscosity at 60°C (140°F), Stokes	Penetration at 25°C (77°F)
A	AC-3	32.7	316	1.5	285	-	1.002	316	494	189
	AC-5	28.8	515	1.9	183	-	1.010	316	788	120
	AC-10	29.3	1136	2.7	93	1.032	1.026	316	2135	62
	AC-20	27.0	1992	4.1	58	1.041	1.028	316	3467	39
B	AC-3	38.3	285	1.5	221	-	1.019	293	630	105
	AC-5	36.6	555	2.0	129	-	1.024	293	1127	75
	AC-10	33.8	986	2.6	82	1.030	1.026	312	2362	48
	AC-20	30.0	1840	3.3	54	-	1.035	302	4469	36
C	AC-5	30.5	585	2.6	175	-	1.020	316	1026	123
	AC-10	48.8	1032	3.3	126	-	1.026	316	1957	81
	AC-20	58.2	1961	4.4	84	-	1.025	316	4126	58
D	AC-3	59.7	303	2.0	270	-	1.011	302	685	148
	AC-5	60.5	468	2.2	189	-	1.014	316	1005	114
	AC-10	59.3	968	3.5	118	-	1.018	316	2190	77
	AC-20	52.7	2035	3.4	66	-	1.032	316	5184	41
G	AC-5	39.9	506	2.1	143	1.020	1.016	303	1184	80
	AC-10	52.8	913	2.5	90	1.023	1.019	305	2418	50
M	AC-5	32.2	494	2.0	166	1.020	1.016	312	902	103
	AC-10	32.6	894	2.6	96	1.024	1.020	315	2399	51
N	AC-5	42.2	505	2.1	149	1.020	1.016	311	1183	81
	AC-10	39.0	1195	3.1	80	1.023	1.019	308	3091	42

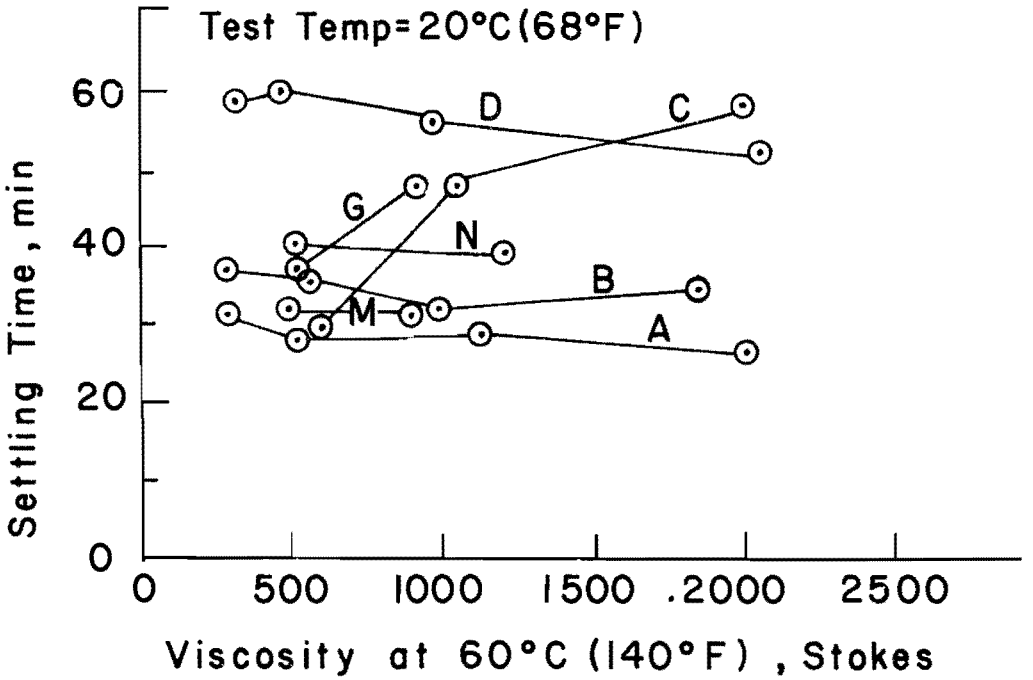

Fig 8. Relationship between viscosity and settling time.

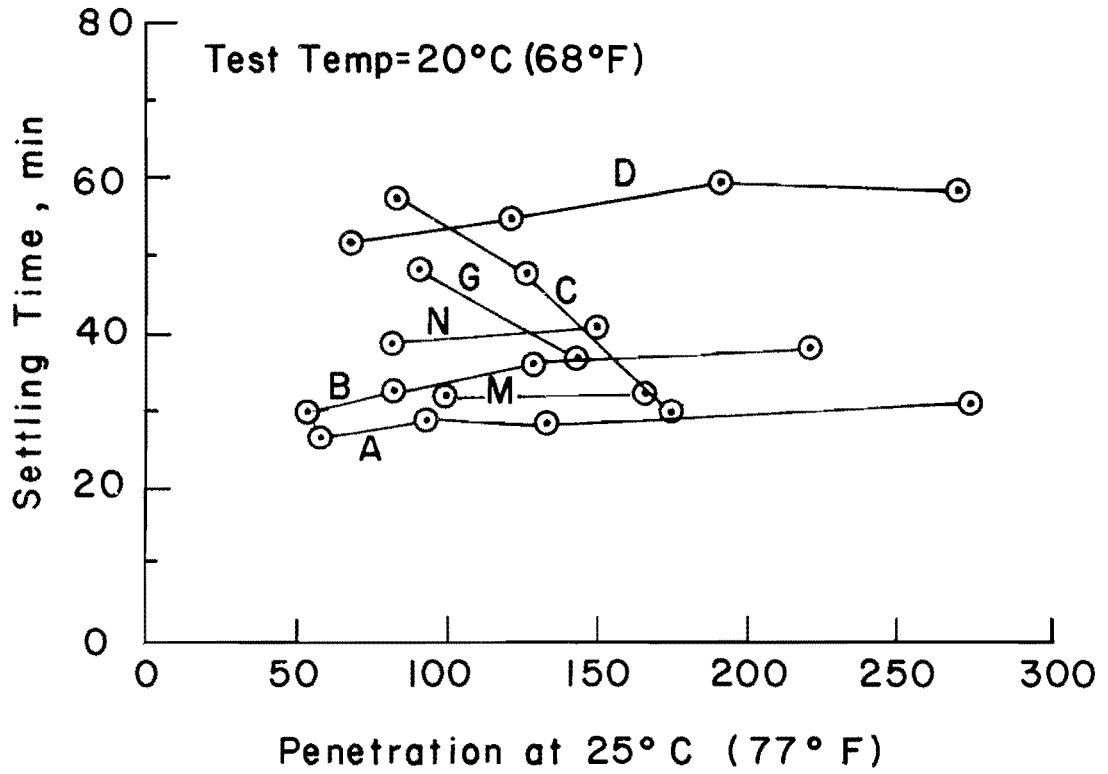

Fig 9. Relationship between penetration and settling time.

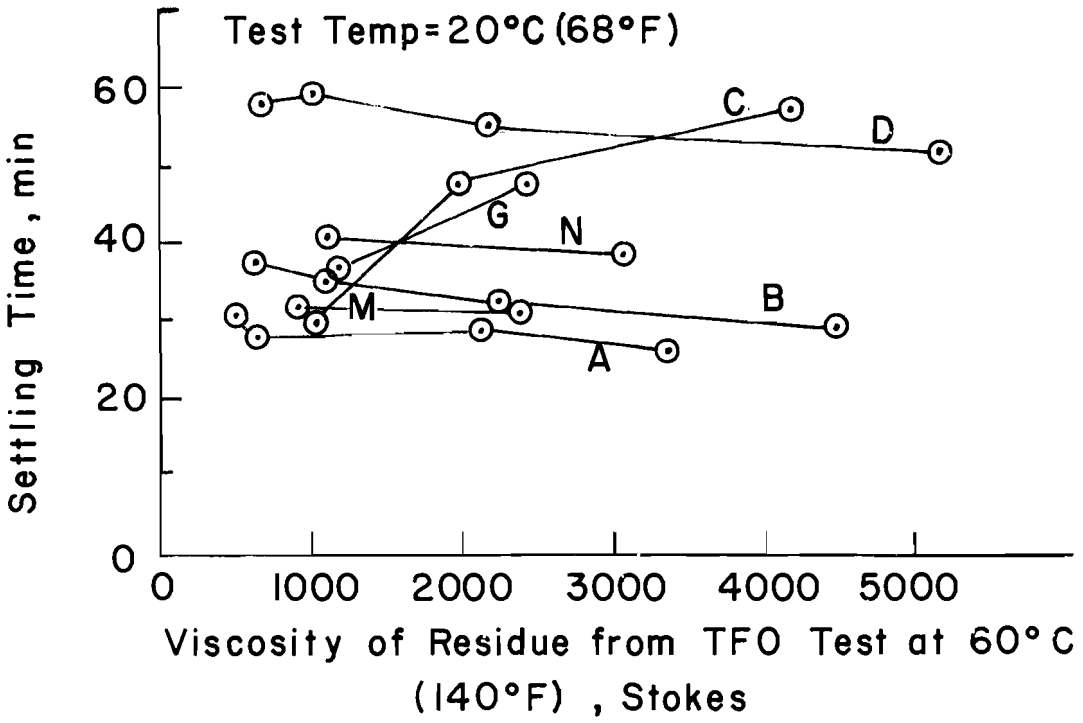

Fig 10. Relationship between viscosity of the residue from TFO test and settling time of virgin asphalt.

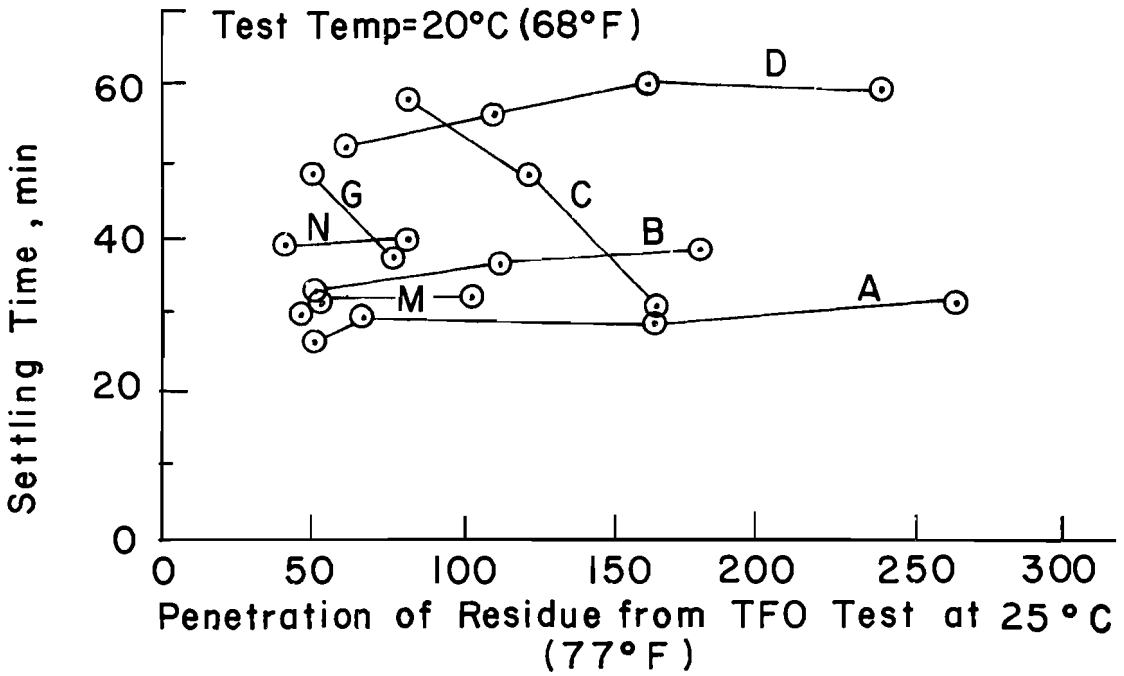

Fig 11. Relationship between penetration of the residue from TFO test and settling time of virgin asphalt.

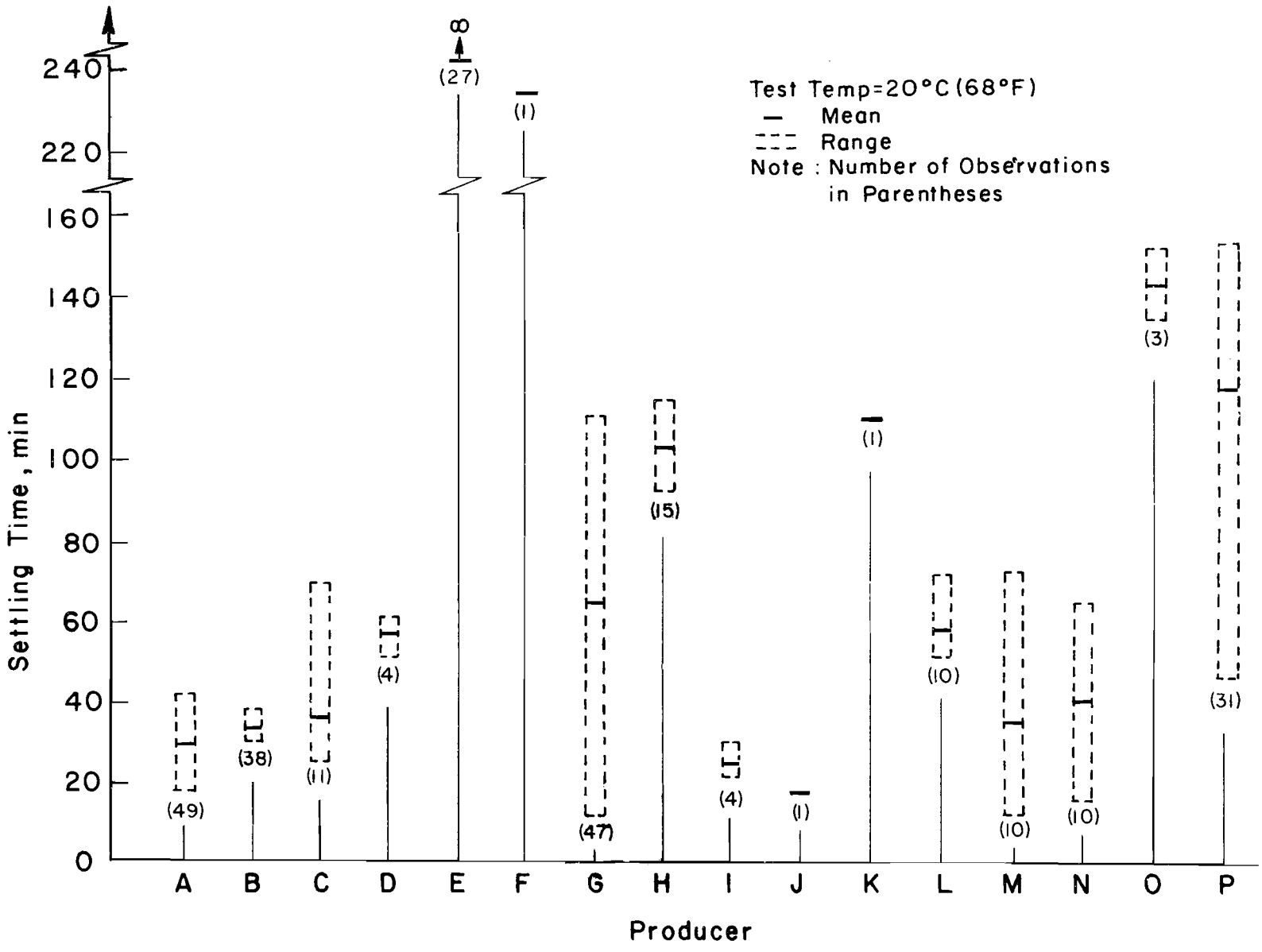

Fig 12. The means and ranges of settling times for various producers.

TABLE 8. SUMMARY OF ASPHALTENE SETTLING TIMES

Producer	Viscosity Grade	Number of Specimens	Asphaltene Settling Time, min			Coeff. of Variation, %
			Extremes	Range	Mean	
A	AC-3	2	24.1 - 32.7	8.6	28.4	21.4
	AC-5	1	- - -	-	28.8	-
	AC-10	24	21.7 - 40.3	18.6	30.3	18.6
	AC-20	22	19.3 - 44.9	25.6	28.4	20.4
	Total	49	19.3 - 44.9	25.6	29.4	19.1
B	AC-3	2	35.0 - 38.3	3.3	36.7	6.4
	AC-5	2	36.6 - 38.0	1.4	37.3	2.7
	AC-10	27	30.0 - 38.3	8.3	33.9	6.6
	AC-20	7	29.4 - 35.4	6.0	31.5	7.8
	Total	38	29.4 - 38.3	8.9	33.8	7.7
C	AC-5	1	- - -	-	30.5	-
	AC-10	2	32.0 - 48.8	16.8	40.4	29.4
	AC-20	8	23.3 - 69.0	45.7	34.8	45.6
	Total	11	23.3 - 69.0	45.7	35.4	39.8
D	AC-3	1	- - -	-	59.7	-
	AC-5	1	- - -	-	60.5	-
	AC-10	1	- - -	-	59.3	-
	AC-20	1	- - -	-	52.7	-
	Total	4	52.7 - 60.5	7.8	58.1	6.2
E*	AC-3	1	* * *	*	∞	*
	AC-5	1	* * *	*	∞	*
	AC-10	13	* * *	*	∞	*
	AC-20	12	* * *	*	∞	*
	Total	27	* * *	*	∞	*

Test temperature = 20°C(68°F)

* No meniscus was observed; all components of the asphalt cement went into solution with the hexane

(continued)

TABLE 8. (Continued)

Producer	Viscosity Grade	Number of Specimens	Asphaltene Settling Time, min			Coeff. of Variation, %
			Extremes	Range	Mean	
F	AC-20	1	- - -	-	235.0	-
G	AC-5	4	12.3 - 67.5	55.2	31.1	80.0
	AC-10	38	18.8 - 105.2	86.4	67.6	34.7
	AC-20	5	22.4 - 112.6	90.2	83.0	42.2
	Total	47	12.3 - 112.6	100.3	66.1	40.8
H	AC-10	7	99.1 - 116.0	16.9	105.5	6.4
	AC-20	8	90.0 - 105.0	15.0	99.3	5.0
	Total	15	90.0 - 116.0	26.0	102.2	6.3
I	AC-10	1	- - -	-	25.3	-
	AC-20	3	20.0 - 28.6	8.6	22.9	21.7
	Total	4	20.0 - 28.6	8.6	23.5	18.0
J	AC-20	1	- - -	-	16.2	-
K	AC-20	1	- - -	-	109.0	-
L	AC-20	10	50.0 - 72.5	22.5	58.1	11.2
M	AC-5	5	18.4 - 66.1	47.7	38.9	54.6
	AC-10	5	11.1 - 73.2	62.1	33.1	72.4
	Total	10	11.1 - 73.2	62.1	36.0	60.0
N	AC-5	5	15.9 - 73.1	57.2	42.2	48.6
	AC-10	5	30.9 - 50.0	19.1	39.6	19.8
	Total	10	15.9 - 73.1	57.2	40.9	35.9
O	AC-20	3	135.8 - 153.8	18.0	143.2	6.6
P	AC-3	1	- - -	-	65.6	-
	AC-10	29	46.3 - 154.5	108.2	118.7	17.8
	AC-20	1	- - -	-	151.4	-
	Total	31	46.3 - 154.5	108.2	118.1	19.8

Test temperature = 20°C(68°F)

The variation of mean settling time between producers ranges from 16.2 to 235.0 minutes (Fig 12). Within the observation period of 132 hours, the asphalt cement from producer E had no observed settling time and was considered to have an infinite settling time.

In Fig 12 and Table 8 it can be seen that the variation of settling times was quite large for some producers; e.g., producers C, G, M, and N had coefficients of variation in excess of 30 percent. Such variation could be related to changes in crude, blending, etc.; however, there is no evidence available from this study to support or reject such a hypothesis.

Although no correlations with viscosity were detected previously, the settling times were evaluated by viscosity grade for each producer. Fig 13 illustrates the mean and range of settling times for the various viscosity grades and producers. However, within the limits of this study, no relationship could be found between settling time and the viscosity grade of each producer. Settling times were producer dependent. Generally the observed settling times for a given producer were independent of asphalt grade; however, the settling time did vary by grade for asphalts from producers G and P.

RELATIONSHIP BETWEEN SETTLING TIME AND VOLUME OF ASPHALTENES

Since the amount of asphaltenes should influence the settling times, a further analysis was conducted to establish the relationship between asphaltene settling time and the estimated volume of asphaltenes. For this analysis the volume of asphaltenes was defined as the reading in milliliters after 24 hours settling. As shown in Fig 14, the relationship was nonlinear and can be described by the following equation:

$$V = -0.14 + 2.25 \ln(ST)$$

where

ST = asphaltene settling time, min, and
V = volume of settled asphaltenes, ml.

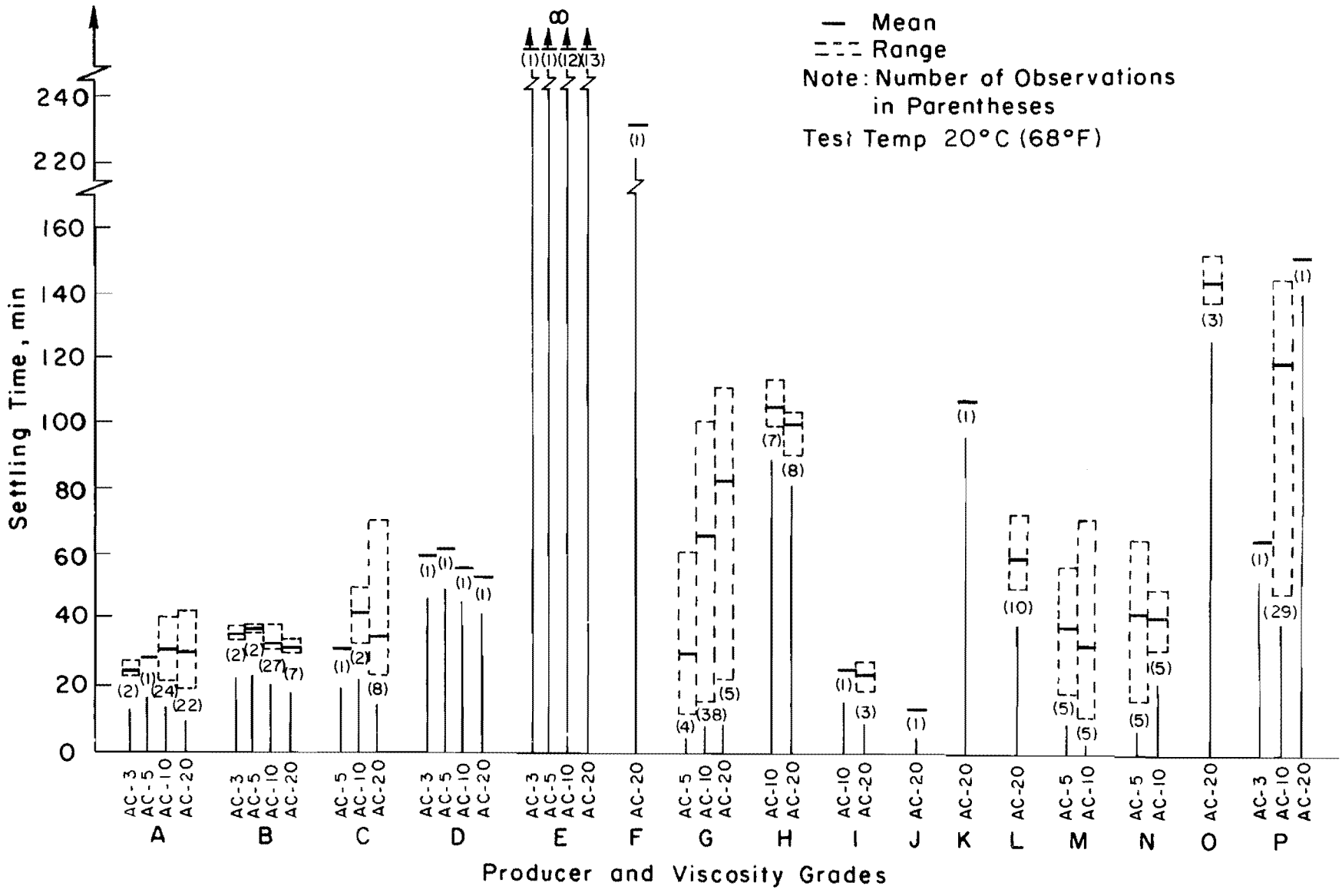

Fig 13. The means and ranges of settling times of various viscosity grades for various producers.

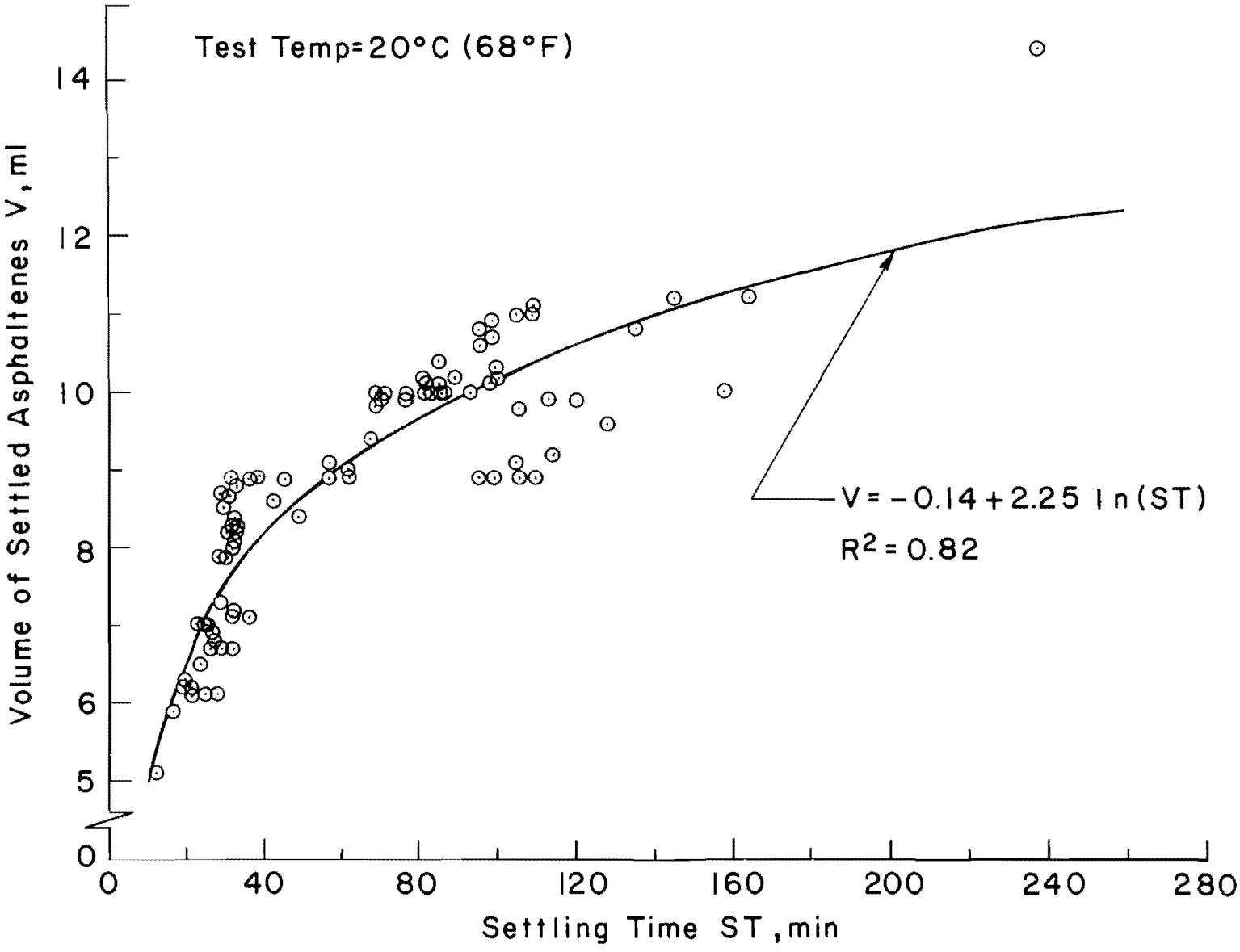

Fig 14. Relationship between asphaltene settling time and volume of settled asphaltenes.

The above relationship was obtained with a coefficient of determination R^2 of 0.82. A more meaningful relationship with less scatter might be obtained by dividing the final volume by the weight of asphaltenes in the sample and then relating volume divided by mass to settling time.

EFFECTS OF ASPHALT MODIFIERS

The two types of asphalt modifiers involved in these tests were anti-stripping agents and asphalt softening agents.

Anti-Stripping Agents

Three asphalt cements were used to evaluate the effect of 14 different anti-stripping agents on settling time. Ten percent, by weight of asphalt cement, of each anti-stripping agent was added to the asphalt-hexane mixture. The resulting settling times are summarized in Table 9 and Fig 15.

Even though no well-defined relationships existed, the asphaltene settling times decreased when anti-stripping agents were added. This observation indicates that the presence of the anti-stripping agents had an effect on test results and the settling times generally decreased for the agents and asphalts tested.

It should be noted that anti-stripping agents $\overline{AC1}$, $\overline{AG4}$, $\overline{AG5}$, and $\overline{AG6}$ apparently caused a residue to remain in the flask and on the stirring bar after the transfer of the mixture into the graduated cylinder.

Asphalt Softening Agents

Tests were conducted to determine the effect of asphalt softening agents on the settling times of virgin asphalts, artificially aged asphalts, and extracted asphalts.

TABLE 9. THE EFFECT OF ANTI-STRIPPING AGENTS ON SETTLING TIME OF VIRGIN ASPHALTS

Producer and Specimen No.	Anti-stripping Agent *	Asphaltene Settling Time, min		
		Original	Modified	Modified/Original,%
A8	$\overline{AA1}$	33.6	26.0	77.4
	$\overline{AB1}$		27.9	83.0
	$\overline{AC1}$		5.0	14.9
	$\overline{AC2}$		20.0	59.5
	$\overline{AD1}$		20.5	61.0
	$\overline{AE1}$		31.2	92.9
	$\overline{AF1}$		25.0	74.4
	$\overline{AF2}$		17.7	52.7
	$\overline{AG1}$		23.6	70.2
	$\overline{AG2}$		28.8	85.7
	$\overline{AG3}$		22.0	65.5
	$\overline{AG4}$		11.5	34.2
	$\overline{AG5}$		13.5	40.2
	$\overline{AG6}$		15.0	44.6
D6	$\overline{AA1}$	62.2	63.7	102.4
	$\overline{AB1}$		51.5	82.8
	$\overline{AC1}$		35.3	56.8
	$\overline{AC2}$		48.3	77.7
	$\overline{AD1}$		38.6	62.1
	$\overline{AE1}$		66.2	106.4
	$\overline{AF1}$		64.0	102.9
	$\overline{AF2}$		41.7	67.0
	$\overline{AG1}$		59.3	95.3
	$\overline{AG2}$		63.8	102.6
	$\overline{AG3}$		59.5	95.7
	$\overline{AG4}$		37.7	60.6
	$\overline{AG5}$		48.0	77.2
	$\overline{AG6}$		51.7	83.1

Test temperature = 20°C(68°F)

*Treated with 10% anti-stripping agents, based on the weight of asphalt

(continued)

TABLE 9. (Continued)

Producer and Specimen No.	Anti-stripping Agent *	Asphaltene Settling Time, min		
		Original	Modified	Modified/Original, %
F32	$\overline{AA1}$	235.0	185.0	78.7
	$\overline{AB1}$		155.0	66.0
	$\overline{AC1}$		135.0	57.4
	$\overline{AC2}$		150.0	63.8
	$\overline{AD1}$		173.5	73.8
	$\overline{AE1}$		178.7	76.0
	$\overline{AF1}$		115.0	48.9
	$\overline{AF2}$		115.4	49.1
	$\overline{AG1}$		160.0	68.1
	$\overline{AG2}$		185.0	78.7
	$\overline{AG3}$		140.0	59.6
	$\overline{AG4}$		141.4	60.2
	$\overline{AG5}$		172.1	73.2
	$\overline{AG6}$		185.0	78.7

Test temperature = 20°C(68°F)

* Treated with 10% anti-stripping agent, based on the weight of asphalt

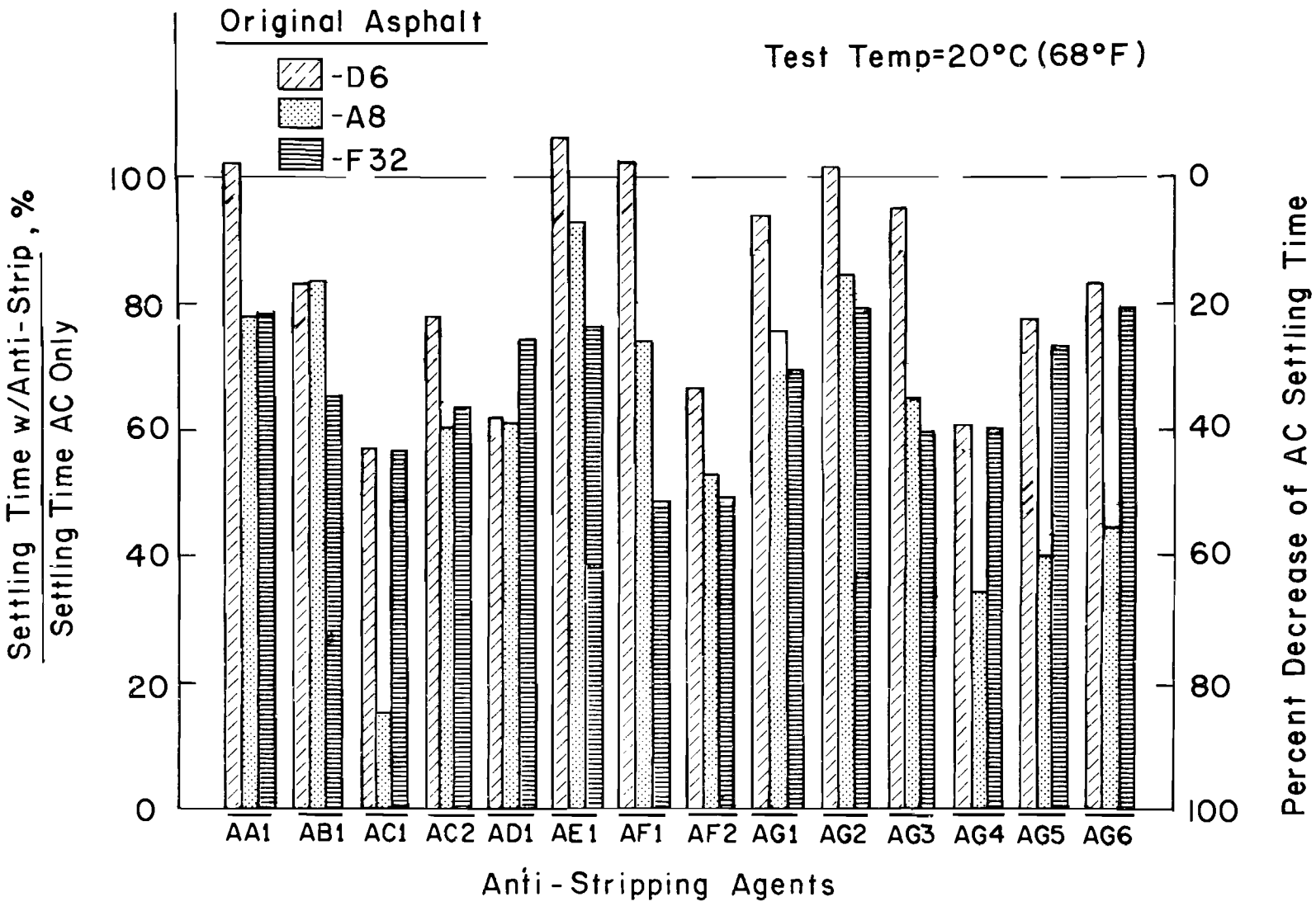

Fig 15. Effects of anti-stripping agents on settling test for various virgin asphalts.

Virgin Asphalt and Artificially Aged Asphalt. One asphalt cement was selected for artificial aging and subsequent determination of the settling times. The asphalt was artificially aged by placing about 5 grams on a small, 3.5-inch-diameter, flat-bottom glass pan in a 121°C (250°F) oven for a specified period of time. Three different commercial asphalt softening agents, identified as RB1, RC1, and RD1, were added to 2.0000 grams of virgin or aged asphalts in the amounts of one and fifteen percent and settling times were determined.

The resulting settling times are summarized in Table 10 and Fig 16. It was observed that (1) no well-defined relationship existed between the settling time and the percent and type of asphalt softening agent (Fig 16) and (2) that for one asphalt the asphaltene settling time increased with the length of aging time (Fig 17).

Extracted Asphalt. The extracted asphalt cement was obtained from cores supplied by District 15, San Antonio, from five locations on the same project. The extractions and testing for physical properties were performed by D-10 of the DHT and are summarized in Table 11.

Four different commercial asphalt softening agents were selected as modifiers, RB1, RC1, RF1, and RG1, and 15 percent by weight was added to the extracted asphalt. Settling times are summarized in Table 11 and Fig 18.

It is assumed that, when asphalt modifiers are added to recovered aged asphalt, longer settling times indicate a more compatible system of asphalt and modifiers (Ref 4). Thus, even though certain asphalt modifier combinations decreased the settling times, the more compatible systems still would be the combinations with the longer settling times.

The ratios of settling time for extracted asphalt with softening agent to initial settling time ranged from 67 to 116 percent. The more compatible systems are presumed to be those with longer settling times (Ref 3).

TABLE 10. THE EFFECTS OF SOFTENING AGENTS ON SETTLING TIME OF VIRGIN AND ARTIFICIALLY AGED ASPHALTS FROM PRODUCER D, SAMPLE 6 (D6)

Hours Aged at 121 °C (250 °F)	Treatment		Asphaltene Settling Time, min
	Asphalt Softening Agent	*Amount Used, %	
0	-	-	62.2
	$\overline{RB1}$	1	66.0
	$\overline{RC1}$	1	72.7
	$\overline{RD1}$	1	66.0
	$\overline{RB1}$	15	71.3
	$\overline{RC1}$	15	65.0
	$\overline{RD1}$	15	60.0
6	-	-	61.2
	$\overline{RB1}$	1	62.7
	$\overline{RC1}$	1	69.8
	$\overline{RD1}$	1	63.7
	$\overline{RB1}$	15	70.0
	$\overline{RC1}$	15	66.0
	$\overline{RD1}$	15	71.9
24	-	-	85.0
	$\overline{RB1}$	1	79.4
	$\overline{RC1}$	1	78.9
	$\overline{RD1}$	1	91.4
	$\overline{RB1}$	15	75.3
	$\overline{RC1}$	15	72.9
	$\overline{RD1}$	15	69.7
48	-	-	100.8
	$\overline{RB1}$	1	93.0
	$\overline{RC1}$	1	93.7
	$\overline{RD1}$	1	109.1
	$\overline{RB1}$	15	94.6
	$\overline{RC1}$	15	71.1
	$\overline{RD1}$	15	83.9

* % based on the weight of asphalt
Test temperature = 20°C(68°F)

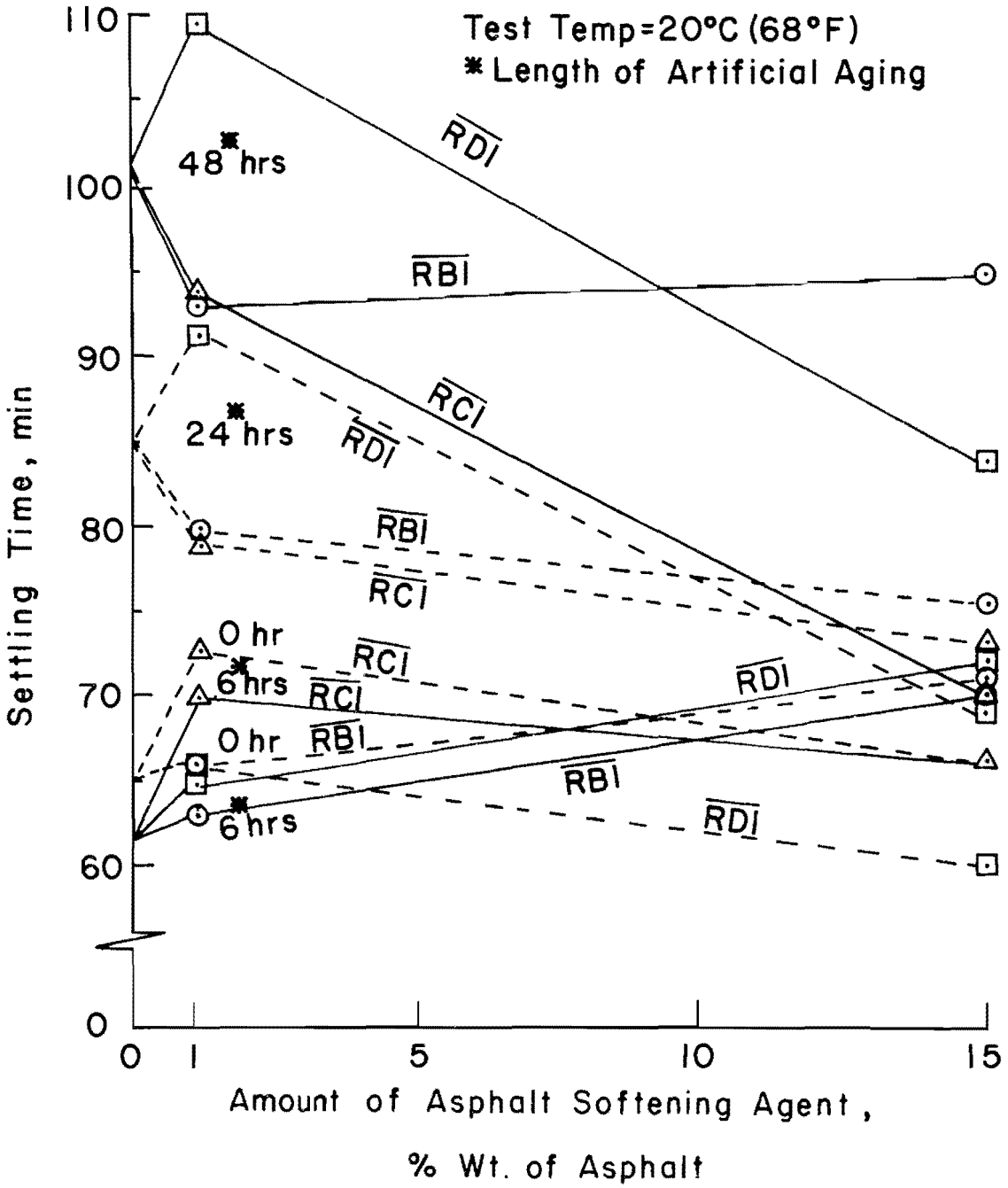

Fig 16. Relationships between the amount of softening agent and settling time for both virgin and artificially aged asphalts.

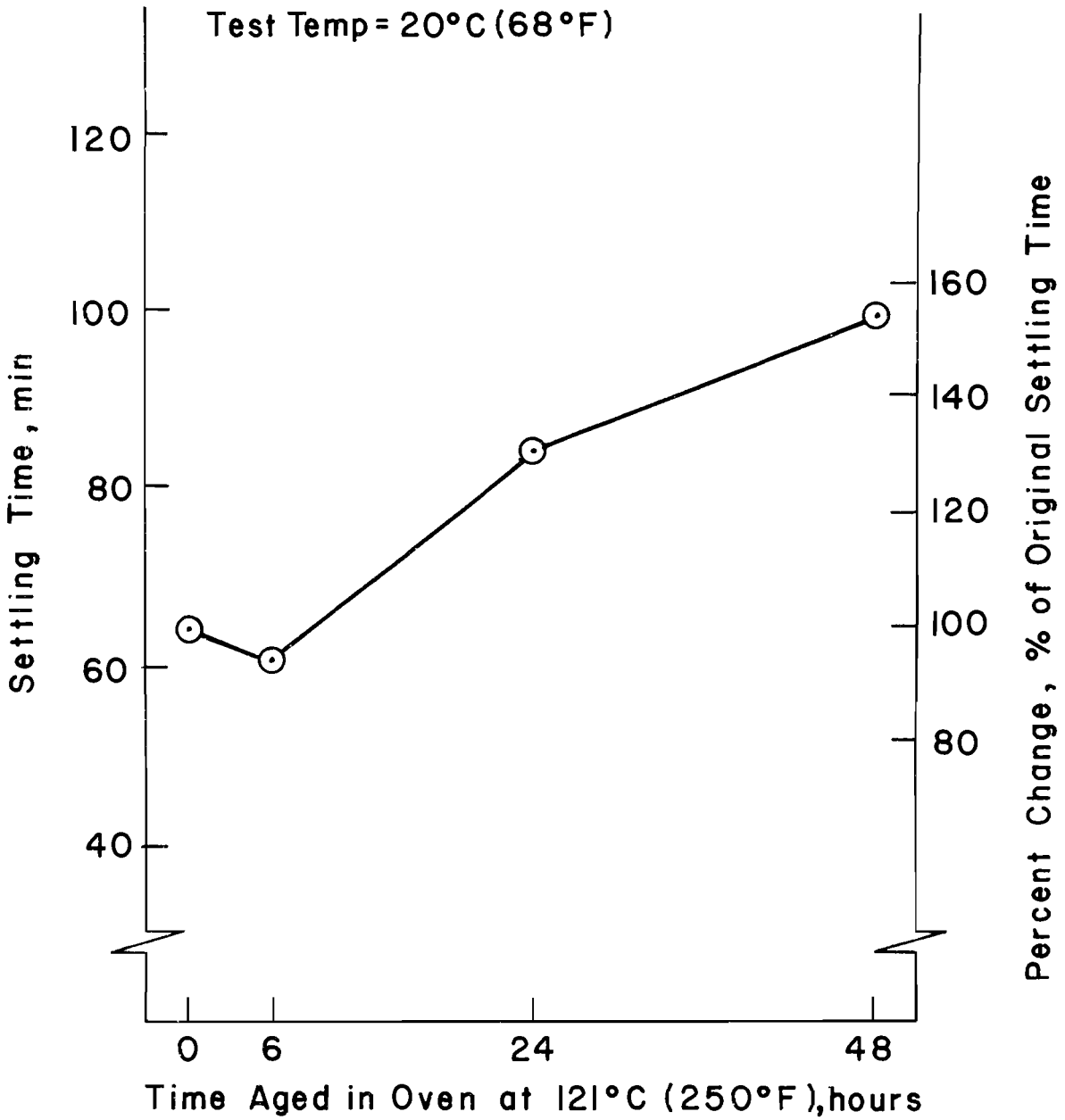

Fig 17. Relationship between time the asphalt was aged in the oven and settling time.

TABLE 11. EFFECTS OF SOFTENING AGENTS ON THE SETTLING TIME OF AN EXTRACTED ASPHALT

Extracted Asphalt			Settling Time for Asphalt and Additive, min								
Specimen Number	Penetration at 25 °C(77 °F)	Viscosity at 60 °C (140 °F), Stokes	None	$\overline{RB1}$		$\overline{RC1}$		$\overline{RF1}$		$\overline{RG1}$	
			Avg	Avg	Ratio	Avg	Ratio	Avg	Ratio	Avg	Ratio
EE184	23	14,195	149	155	104	150	101	108	72	145	97
EE185	-	-	120	135	112	119	99	88	73	125	104
EE187	20	16,162	125	145	116	139	111	98	79	137	110
EE189	25	7,702	132	128	97	129	98	98	75	128	97
EE190	17	24,007	109	108	99	105	96	73	67	105	96
Average	21	15,518	127	134	106	128	101	93	73	128	101

$$\text{Ratio} = \frac{\text{Settling time with additive}}{\text{Settling time without additive}} \times 100\%$$

Test temperature = 20°C(68°F)

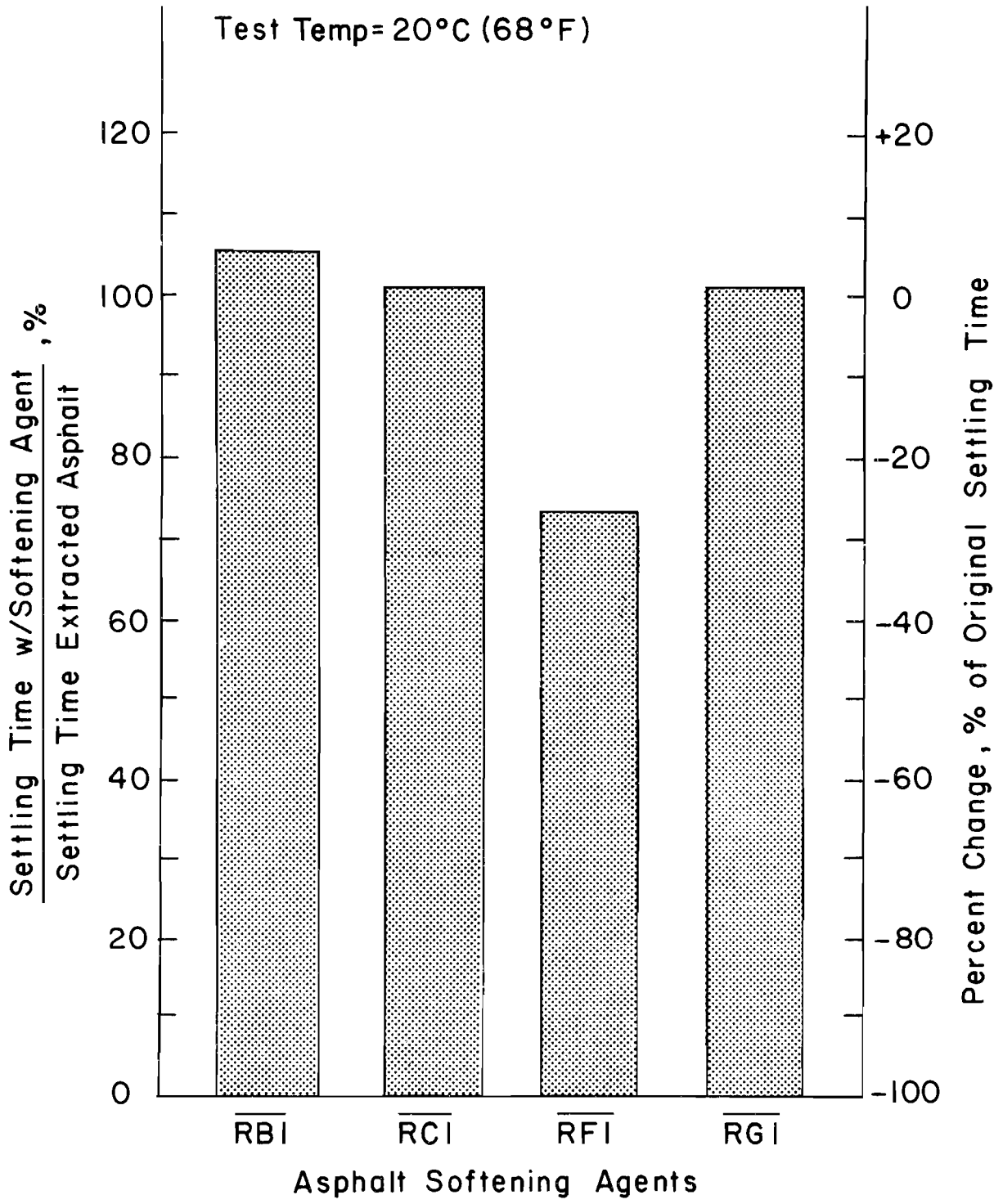

Fig 18. Effect of asphalt softening agents on settling time for an average of 5 samples of an extracted asphalt.

CHAPTER 4. CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations based on the findings of this investigation are summarized below. The primary purposes of this study were (1) to evaluate the repeatability of the test, the effect of various test variables, and the effect of various modifiers; and (2) to investigate the relationships between settling time and the characteristics of the asphalt cements.

CONCLUSIONS

The test is quite easy to conduct and quantitative test values can be obtained. Nevertheless, it is felt that a great deal of additional work will be required if the test is to have any practical value to practicing engineers. The complexity of the asphaltene, maltene, hexane mixtures and the interaction of these components and their characteristics would appear to have a very definite effect on the test results and their meaning. Additional work on interpretation of test results will be required before the test can be used routinely.

Repeatability and Operators

(1) The repeatability of the test values was fair and it was essentially the same for different operators and over a period of time

   (a) The coefficients of variation of settling times ranged from 2.8 to 9.2 percent for operator 1 and 4.9 to 9.4 for operator 2 in simultaneous tests.

(b) The coefficient of variation of settling times varied from 2.7 to 5.9 for one operator conducting tests over a period of ten days.

(2) A definite operator effect was detected with one of the operators consistently obtaining shorter settling times. This was attributed to the times required to transfer the mixture from the stirring flask to the graduated cylinder.

Test Variables

(3) The amount of asphalt (1.9000, 1.9900, 2.0000, 2.0100, and 2.1000 grams) in the mixtures had no practical effect on the settling times in this study. It is felt that the precision should be 2.00 $\pm$ .01 grams.

(4) Heating the asphalt from room temperature to 82°C (180°F) during mixture preparation had no effect on the test results nor did repeated heating. Nevertheless, heating of the asphalt should be minimized.

(5) Testing temperature produced a significant effect on the asphaltene settling time the settling times were shorter at higher temperatures. Consideration probably should be given to conducting the test at room temperature, approximately 24-25°C (75-77°F).

Relationship to Asphalt Characteristics

(6) The settling time varied significantly with producer. In fact, for the asphalts tested in this study the producer of asphalt was the only factor which affected settling time.

(7) No relationships were found between the settling time and specification type asphalt characteristics, such as viscosity, penetration, specific gravity, and flash point.

(8) The following equation was found to approximate the relationship between settling time and the volume of the settled asphaltene after 24 hours settling:

$$V = -0.14 + 2.25 \ln(ST)$$

$$R^2 = \text{coefficient of determination} = 0.82$$

where

ST = settling time, min., and

V = volume of settled asphaltenes, ml .

Other factors such as the density of the asphaltenes in the mixture probably should be considered in the above relationship.

Effects of Asphalt Modifiers

(9) Settling times decreased with respect to virgin asphalt when 10 percent anti-stripping agent was added.

(10) The settling time of asphalt cement increased with increased time of aging in an oven at 121°C (250°F).

(11) No well-defined relationship existed between the settling time and the addition of asphalt softening agent for either the virgin or the artificially aged asphalt; however, the settling time had a tendency to decrease when 15 percent of asphalt softening agent was added.

(12) The asphalt softening agents were not equally effective as asphaltene dispersants for the extracted asphalts. This agreed with the findings previously reported by Plancher et al.

RECOMMENDATIONS

Test Procedure

(1) It is recommended that 2.00 grams with an accuracy of ± 0.01 gram of asphalt cement be used in the preparation of the asphalt cement-hexane mixture.

(2) The asphalt cement should not be heated during mixture preparation.

(3) The testing temperature for the asphaltene settling test should be closely controlled and probably requires a temperature chamber or water bath.

(4) Timing should start 20 seconds after stirring is complete. The transfer of the asphalt-hexane mixture should be completed within 20 seconds.

(5) Consideration should be given to eliminating the 10 ml wash since it changes the mixture concentration in the upper part of the cylinder and is responsible for the major portion of the transfer time. It is also felt that the amount of residue left behind probably is not important.

Research

(6) If the test method is to have practical value, additional study should be made to determine the significance and meaning of the test results. This would include rheological study as well as studies relating test values to field performance.

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3. Plancher, H., A. J. Hoiberg, S. C. Suhaka, and J. C. Petersen, "A Settling Test to Evaluate the Relative Degree of Dispersion of Asphaltenes," Proceedings, Association of Asphalt Paving Technologists, Vol 48, 1979, pp. 351-374.

4. Plancher, H., private communication to authors, June 5, 1981, comments in review of CTR Report No. 253-2, Laramie, Wyoming.

APPENDIX A

TEST EQUIPMENT, SUPPLIES, AND PROCEDURE

APPENDIX A. TEST EQUIPMENT, SUPPLIES, AND PROCEDURE

TEST EQUIPMENT AND SUPPLIES

The following equipment and supplies are required to conduct the asphaltene settling test:

(1) 100-ml round-bottom boiling flask with a 24/40 ground glass stopper;
(2) magnetic stirrer;
(3) magnetic stirring bar, 7.9 by 25.4 mm (5/16 by 1 in.);
(4) 50-ml syringe graduated in 5-ml increments, with a number 15 needle (60° bend in needle);
(5) 10-ml syringe graduated in 0.2-ml increments, with a number 15 needle (60° bend in needle);
(6) normal hexane, pure grade, 99 mole percent;
(7) ring stand with flask clamp;
(8) small horseshoe magnet;
(9) cork ring, 76 mm (3 in.) in diameter;
(10) glass funnel, 64 mm (2.5 in.) in diameter with 25.4-mm (1-in.) stem;
(11) 50-ml glass cylinder graduated in 1-ml increments, 25.4 by 254 mm (1 by 10 in.), with a 24/40 ground glass stopper;
(12) stopwatch;
(13) high-intensity light; and
(14) controlled temperature environment at 20°C (68°F).

ASPHALTENE SETTLING TEST PROCEDURE

The detailed testing procedure is composed of

(1) mixture preparation,
(2) transfer of mixture, and
(3) settling time determination.

Mixture Preparation

(1) Weigh 2.0000 grams* of asphalt at room temperature and place on lower one-third of a 100-ml round-bottom flask. Caution should be taken not to contaminate the specimen nor to obtain surface asphalt that might be oxidized. The objective is to secure a representative sample.
(2) Suspend the flask above a magnetic stirrer in a 20°C (68°F) constant-temperature environment (temperature chamber or water bath).
(3) Add 50 ml of n-hexane into the flask using a 50-ml syringe graduated in 5-ml increments.
(4) Place a magnetic stirring bar, 7.9 by 25.4 mm (5/16 by 1 in.), in the flask.
(5) Wet a 24/40 ground glass stopper with n-hexane and seal the flask.
(6) Adjust the speed of the magnetic stirrer to create approximately a 12.7-mm (0.5-in.) vortex in the center of the flask. Splashing the solution onto the upper region of the flask by too vigorous stirring should be avoided.
(7) After stirring for 45 minutes, wipe the inside of the flask to dislodge the thin film of the solution by moving the stirring bar up and down the sides of the flask with the aid of an external horseshoe magnet.

*Based on the results of this study, it is recommended that 2.00 ± 0.01 g of asphalt be used.

(8) Repeat the wiping action after 7 to 9 hours of stirring to ensure the proper dissolution of the asphalt.

(9) Continue stirring the mixture for a total of 20 hours.

Transfer of Mixture

Note: The transfer of mixture should not be performed on the table where the magnetic stirring is occurring in order to avoid any vibration which might affect the test results.

(1) Place a 50-ml graduated cylinder with 1-ml divisions and a funnel in its neck in the 20°C (68°F) constant-temperature chamber.

(2) Remove the flask containing the mixture from the magnetic stirrer.

(3) Wipe the inside wall of the flask containing the mixture with the stirring bar, using the external horseshoe magnet as previously described.

(4) Place a cork ring 76 mm (3 in.) in diameter on top of the magnetic stirrer.

(5) Place the flask containing the mixture on the cork ring.

(6) Fill a 10-ml syringe graduated in 0.2-ml increments with 10 ml of n-hexane, and then loosen the stopper of the flask containing the mixture.

Note: Since the test is based on the rate at which the asphaltene settles by the influence of gravity through a hexane-maltene mixture, the duration of the transferring procedure is critical and should be the same for all transfers. It is suggested that steps 7 to 10 should be completed within 30 seconds* (Ref 3).

(7) Start the stopwatch and immediately remove the stopper from the flask. Empty the mixture through the funnel including the stirring bar into the 50-ml graduated cylinder. The stirring bar will remain in the funnel.

*Based on the results of this study, it is recommended that this transfer time be decreased to 20 seconds in order to reduce the error between operators.

(8) Use approximately 1/2 of the 10 ml of n-hexane in the syringe to rinse the residue from the flask; pour it into the graduated cylinder.

(9) With the remaining n-hexane in the syringe rinse the residue from the funnel and the stirring bar.

(10) Quickly seal the graduated cylinder with a hexane-wet 24/40 ground glass stopper.

Settling Time Determination

(1) At 5-minute intervals record the location of the meniscus of the descending asphaltenes, estimating to the nearest 0.1 ml by using a high-intensity light to aid in reading.

(2) Record the first reading when the meniscus of the descending asphaltene is at 50 ml or less. Do not record any reading above the 50 ml.

(3) Continue reading until the meniscus drops to the 10-ml to 15-ml level until the rate of settling is not significant. Care should be taken (a) not to disturb the graduated cylinder and (b) not to hold the high-intensity light too close to the graduated cylinder for too long a period of time when taking the readings.

(4) Asphaltene settling time of the asphalt is defined as the time in minutes required for the meniscus of the asphaltene to descend to the 25-ml level in the graduated cylinder (Ref 3). Figure A.1 shows the typical asphaltene settling curve.

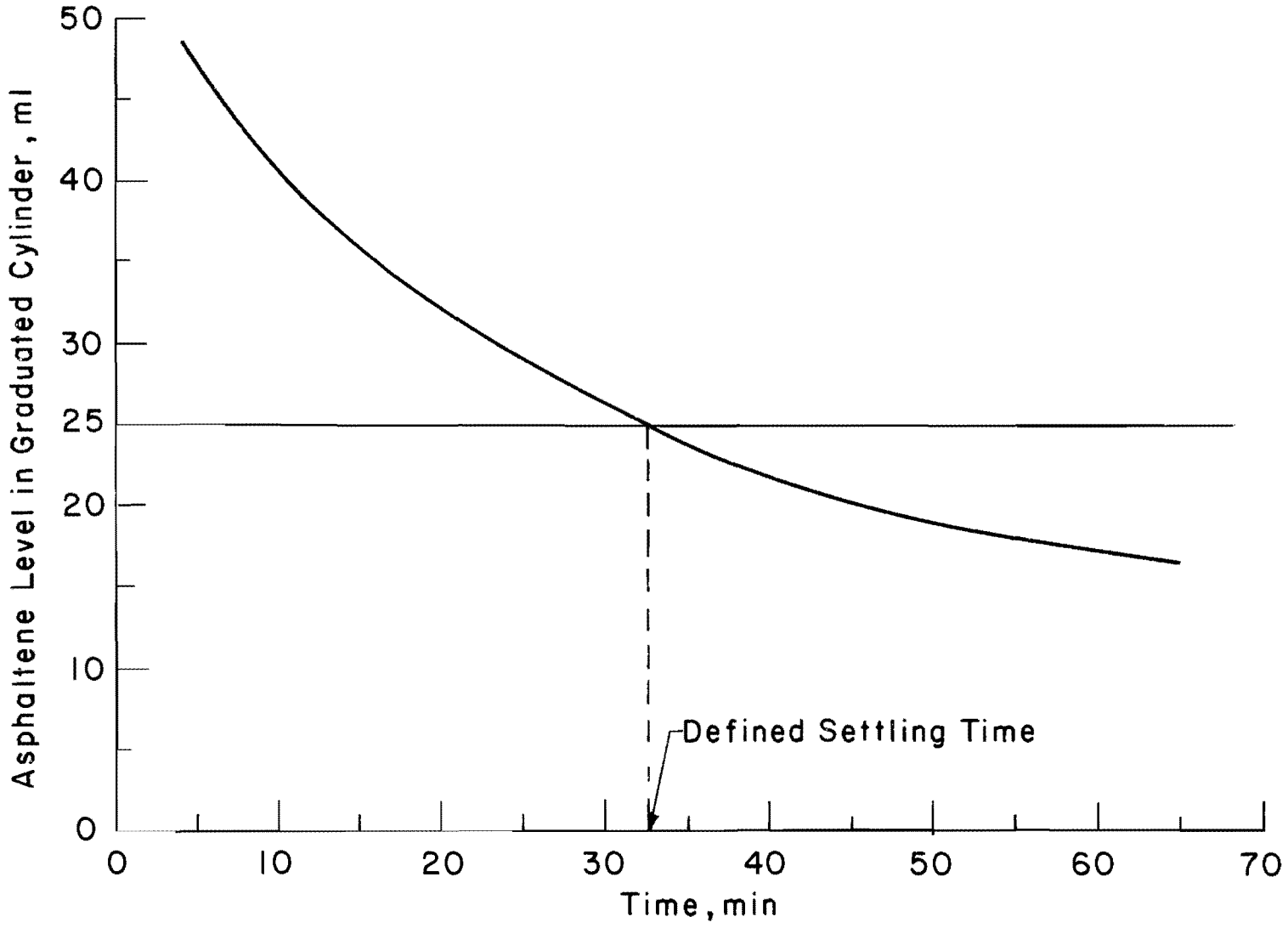

Fig A1. Typical asphaltene settling curve.

APPENDIX B

EXPERIMENTAL DESIGNS

APPENDIX B. EXPERIMENTAL DESIGNS

TABLE B.1. EXPERIMENTAL DESIGN FOR REPEATABILITY OF ASPHALTENE SETTLING TEST

Producer and Specimen Number	Asphalt Grade	Simultaneous Tests		Daily Tests
		Operator 1	Operator 2	Operator 1
A9	AC-5	10	10	10
A53	AC-10	-	-	10
A249	AC-3	9	-	-
B15	AC-20	10	10	10
C20	AC-5	10	10	10
D4	AC-3	10	10	10
D5	AC-5	10	10	10
G178	AC-10	-	-	10
H245	AC-10	9	-	-
P170	AC-10	-	-	10

TABLE B.2. EXPERIMENTAL DESIGN FOR THE EVALUATION OF THE RELATIONSHIPS BETWEEN THE SETTLING TIME AND ASPHALT CHARACTERISTICS

Producer	Asphalt Grade	Number of Samples
A	AC-3	2
	AC-5	1
	AC-10	24
	AC-20	22
B	AC-3	2
	AC-5	2
	AC-10	27
	AC-20	7
C	AC-5	1
	AC-10	2
	AC-20	8
D	AC-3	1
	AC-5	1
	AC-10	1
	AC-20	1
E	AC-3	1
	AC-5	1
	AC-10	13
	AC-20	12
F	AC-20	1
G	AC-5	4
	AC-10	38
	AC-20	5
H	AC-10	7
	AC-20	8
I	AC-10	1
	AC-20	3
J	AC-20	1
K	AC-20	1
L	AC-20	10
M	AC-5	5
	AC-10	5
N	AC-5	5
	AC-10	5
O	AC-20	3
P	AC-3	1
	AC-10	29
	AC-20	1
TOTAL		262

TABLE B.3. EXPERIMENTAL DESIGN FOR THE EVALUATION OF THE EFFECT OF ASPHALT SOFTENING AGENTS ON SETTLING TIME FOR AN ARTIFICIALLY AGED AC-10 ASPHALT DESIGNATED AS D6

Hours Aged at 250° F	% by Weight of Asphalt	Asphalt Softening Agent			
		None	$\overline{\text{RB1}}$	$\overline{\text{RC1}}$	$\overline{\text{RD1}}$
0	0	1	-	-	-
	1	-	1	1	1
	15	-	1	1	1
6	0	2	-	-	-
	1	-	2	2	2
	15	-	1	1	1
24	0	2	-	-	-
	1	-	2	2	2
	15	-	1	1	1
48	0	2	-	-	-
	1	-	2	2	1
	15	-	1	1	1