NATIONAL BUREAU OF STANDARDS REPORT

5935

RELATION OF RATE OF COMPONENT CHANGES IN
ASPHALTS TO ACCELERATED DURABILITY

by

John P. Falzone

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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John P. Falzone

Research Associate
Asphalt Roofing Industry Bureau

Floor, Roof and Wall Coverings Section
Building Technology Division

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ABSTRACT

Twenty asphalts from various sources of crude were separated chromatographically both before weathering and at final failure in the 51-9C cycle of the Atlas Weather-O-Meter.

By plotting the percent increase of the asphaltenes per day of exposure versus the durability of the given asphalt, a graphic relationship was obtained. Similar handling of rate changes of asphaltenes plus weight loss or rate changes in total oily constituents versus accelerated durabilities gave rise to related curves. Use of the asphaltene content was found to be desirable because of its simplicity and preciseness from a laboratory point of view.

The results indicate that a method for the rapid evaluation of the relative accelerated durabilities of a group of asphalts can be developed.

Some important variables uncovered during the accumulation of the data are discussed.

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1. INTRODUCTION

During the investigation of the filtration rate of the n-pentane solubles of a coating asphalt through its insolubles (asphaltenes), it was necessary to recheck the accelerated durabilities of the twenty-two asphalts being studied, since the latter had been in storage for over two years. Analysis of weight loss data subsequently acquired indicated a closer relationship to durability than had been previously suspected. This encouraging development logically indicated that a component rate of change study might prove more fruitful and reliable than one associated with the degradation products.

This report summarizes the manner by which this necessary information was obtained, the recognized variables in the procedures employed and the promising conclusions drawn from the analysis of the results.

2. ASPHALTS

Twenty asphalts representing east and west coast and midcontinental sources of crude were used. Two additional asphalts whose durability had been determined could not be considered since a sample of each prior to weathering was not available. These were C810 and C1342 and were derived from west coast crudes.

3. PROCEDURES

Accelerated durabilities and component separations were determined for each asphalt. The latter was done by the method of Kleinschmidt (1)[1/]. The coatings for exposure in the 51-9C cycle were prepared by the hydraulic press method (2). Spark inspections were carried out twice weekly and in the manner recently reported (3).

4. RESULTS AND DISCUSSION

The desired data obtained for the twenty asphalts is summarized in Table 1.

If the rate of change per day for the asphaltene component is plotted against the durability of that particular asphalt, a fairly smooth curve is obtained, as in Figure 1.

Figures 2 and 3 were obtained by similarly employing (a) the increase per day of durability for the sum of asphaltenes and weight loss, and (b) the rate of decrease per day of total oils.

1/ Figures in parentheses indicate literature references at the end of this report.

TABLE 1.

Asphalt and Components	Final Failure	Before Weathering	Durability (51-9C)	Total Change in Fraction	Change in Fraction
	%	%	Days	%	%/Day
C1175 (1)			23		
Asphaltenes	48.0	39.8		8.2	0.356
White Oils	21.5	26.8		5.3	0.230
Dark Oils	12.6	22.5		9.9	0.430
Resins	10.3	10.6		0.3	
Cleanup	0.0	0.0		0.0	
Weight Loss	7.5	----		7.5	0.326
Recovery	99.9	99.7			
Middle East (3)			42		
Asphaltenes	52.7	46.4		6.3	0.150
White Oils	12.9	16.8		3.9	0.093
Dark Oils	15.3	25.4		10.1	0.241
Resins	9.1	10.1		1.0	
Cleanup	0.2	0.3		0.1	
Weight Loss	9.3	----		9.3	0.221
Recovery	99.5	99.0			
Talco (4)			34		
Asphaltenes	48.7	41.6		7.1	0.208
White Oils	12.8	19.0		6.2	0.182
Dark Oils	19.4	32.2		12.8	0.376
Resins	9.5	7.2		2.3	
Cleanup	----	0.1		----	
Weight Loss	9.0	----		9.0	0.265
Recovery	99.4	100.1			
C-210 (4)			37		
Asphaltenes	44.6	39.1		5.5	0.149
White Oils	19.7	26.8		7.1	0.192
Dark Oils	11.3	21.6		10.3	0.279
Resins	10.3	12.7		2.4	
Cleanup	0.0	0.2		----	
Weight Loss	13.3	----		13.3	0.359
Recovery	99.2	100.4			
Envoy (2)			30		
Asphaltenes	48.0	40.6		7.4	0.247
White Oils	19.4	26.4		7.0	0.233
Dark Oils	13.1	23.0		9.9	0.330
Resins	11.7	10.2		1.5	
Cleanup	0.1	0.0		----	
Weight Loss	8.8	----		8.8	0.293
Recovery	100.1	100.2			

(Continued on next page)

TABLE 1. (Continued) - 2

Asphalt and Components	Final Failure	Before Weathering	Durability (51-9C)	Total Change in Fraction	Change in Fraction
	%	%	Days	%	%/Day
Lag. (4)			61		
Asphaltenes	48.1	40.5		7.6	0.125
White Oils	14.9	19.1		4.2	0.069
Dark Oils	18.4	30.0		11.6	0.190
Resins	12.1	10.3		1.8	
Cleanup	0.1	0.2		0.1	
Weight Loss	6.9	----		6.9	0.113
Recovery	100.5	100.1			
East Ven. (3)			50		
Asphaltenes	43.7	37.2		6.5	0.130
White Oils	21.5	25.4		3.9	0.078
Dark Oils	17.3	29.0		11.7	0.234
Resins	9.8	9.4		0.4	
Cleanup	----	0.2		----	
Weight Loss	8.0	----		8.0	0.160
Recovery	100.3	101.2			
Ambit (4)			34		
Asphaltenes	50.3	38.3		12.0	0.353
White Oils	14.4	21.2		6.8	0.200
Dark Oils	14.0	29.6		15.6	0.459
Resins	9.5	10.0		0.5	
Cleanup	0.1	0.2		0.1	
Weight Loss	12.0	----		12.0	0.353
Recovery	100.3	99.3			
V-200 (2)			64		
Asphaltenes	44.9	38.3		6.6	0.103
White Oils	15.2	20.7		5.5	0.089
Dark Oils	17.5	30.7		13.2	0.206
Resins	11.3	10.1		1.2	
Cleanup	0.3	0.5		0.2	
Weight Loss	10.6	----		10.6	0.166
Recovery	99.8	99.3			
Cat. (2)			88		
Asphaltenes	46.0	38.1		7.9	0.090
White Oils	15.6	22.1		6.5	0.074
Dark Oils	15.8	31.6		15.8	0.180
Resins	10.5	8.2		2.3	
Cleanup	----	0.3		----	
Weight Loss	12.5	----		12.5	0.142
Recovery	100.4	100.3			

(Continued on next page)

TABLE 1. (Continued) - 3

Asphalt and Components	Final Failure	Before Weathering	Durability (51-9C)	Total Change in Fraction	Change in Fraction
	%	%	Days	%	%/Day
Shallow H_2O (4)			63		
Asphaltenes	42.1	35.8		6.3	0.098
White Oils	16.3	20.0		3.7	0.058
Dark Oils	18.8	33.5		14.7	0.230
Resins	9.5	8.4		0.7	
Cleanup	0.4	0.4		----	
Weight Loss	12.9	----		12.9	0.205
Recovery	100.0	98.1			
Midcont. 200 (4)			87		
Asphaltenes	45.0	39.6		5.4	0.062
White Oils	16.8	22.8		6.0	0.068
Dark Oils	15.7	26.5		10.8	0.124
Resins	8.9	10.0		1.1	
Cleanup	0.5	0.7		0.2	
Weight Loss	12.8	----		12.8	0.147
Recovery	99.7	99.6			
Louisiana (3)			64		
Asphaltenes	42.5	36.9		6.6	0.103
White Oils	16.6	21.5		4.9	0.077
Dark Oils	20.0	31.5		11.5	0.180
Resins	10.9	9.7		1.2	
Cleanup	0.4	0.8		0.4	
Weight Loss	9.1	----		9.1	0.142
Recovery	99.5	100.4			
Columbia (1)			70		
Asphaltenes	41.9	36.7		5.2	0.074
White Oils	20.8	28.8		8.0	0.114
Dark Oils	14.6	25.6		11.0	0.157
Resins	8.9	8.7		0.2	
Cleanup	0.4	0.3		0.1	
Weight Loss	13.4	----		13.4	0.192
Recovery	100.0	100.1			
Kansas-I (1)			79		
Asphaltenes	44.3	39.6		4.7	0.060
White Oils	15.5	22.5		7.0	0.089
Dark Oils	17.5	27.9		10.4	0.132
Resins	8.5	8.2		0.3	
Cleanup	1.4	0.5		0.9	
Weight Loss	11.7	----		11.7	0.148
Recovery	98.9	98.7			

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TABLE 1. (Continued) - 4

Asphalt and Components	Final Failure	Before Weathering	Durability (51-9C)	Total Change in Fraction	Change in Fraction
	%	%	Days	%	%/Day
Kansas-II (3)			86		
Asphaltenes	43.9	35.3		8.6	0.100
White Oils	13.4	24.1		10.7	0.124
Dark Oils	13.5	26.2		12.7	0.148
Resins	13.2	11.9		1.3	
Cleanup	1.2	0.5		0.7	
Weight Loss	13.9	----		13.9	0.162
Recovery	99.1	98.0			
Union (3)			43		
Asphaltenes	48.7	43.3		5.4	0.126
White Oils	15.6	24.1		8.5	0.198
Dark Oils	13.0	23.6		10.6	0.247
Resins	10.4	9.1		1.3	
Cleanup	0.0	0.1		0.1	
Weight Loss	13.2	----		13.2	0.307
Recovery	100.9	100.2			
Mexican (2)			76		
Asphaltenes	55.7	42.5		13.2	0.174
White Oils	11.1	16.2		5.1	0.067
Dark Oils	14.2	33.2		19.0	0.250
Resins	6.3	7.1		0.8	
Cleanup	2.0	0.5		1.5	
Weight Loss	9.6	----		9.6	0.126
Recovery	98.9	99.5			
Oklahoma (4)			115		
Asphaltenes	42.5	36.0		6.5	0.056
White Oils	13.7	20.9		7.2	0.063
Dark Oils	15.2	30.9		15.7	0.136
Resins	11.3	10.5		0.8	
Cleanup	1.0	1.2		0.2	
Weight Loss	16.1	----		16.1	0.140
Recovery	99.8	99.5		----	
Shell (4)			67		
Asphaltenes	47.3	40.8		6.5	0.097
White Oils	13.8	26.0		12.2	0.182
Dark Oils	12.3	22.9		10.6	0.158
Resins	10.2	8.7		1.5	
Cleanup	0.1	1.8		1.7	
Weight Loss	16.8	----		16.8	0.251
Recovery	100.5	100.2			

Several important variables which are discussed in the next section restrict more exact quantitative interpretation of the results. Nonetheless, the following information may be validly derived from a study of the graphs:

(1) Irrespective of the source of crude, a fairly good correlation exists between the rate of formation of asphaltenes and accelerated durability. Alternatively, the rate of decrease of total oils or the rate of increase of asphaltenes plus weight loss versus accelerated durability may be used, the latter yielding similar relationships which align the asphalts, generally, in the same relative positions obtained by employing the former.

(2) The rate of increase of asphaltenes plus weight loss is approximately equal to the rate of decrease of total oils. Consequently, Figures 2 and 3 are virtually the same.

(3) The slope of the curves in all three figures is steepest in the region where the poorest weatherers are found. Consequently, sharper end-points and good reproducibility can be expected for coatings that fail in roughly 50 days or less. Conversely, the gradual change in the slope of the curves in the region representing the better weathering asphalts shows that the durabilities are extremely sensitive to small differences in rates of change. Much poorer precision and reproducibility can be expected then for those asphalts having durabilities of approximately sixty days or more. In general, this observation is in agreement with actual practice. This effect can be minimized to some extent by re-emphasizing temperature control during exposure and rigid adherence to a standardized inspection procedure.

5. VARIABLES PRESENT

During the normal development of this approach, it became evident that two important factors were contributing heavily to the uncertainty and scatter that was present in the data.

The first of these was concerned with the fact that the spark inspection procedure was not sufficiently standardized to yield comparable and reasonably reproducible failure points. Although the proper steps have now been taken to correct this condition, about half of the durabilities in this report were obtained without the benefit of the revised procedure.

A second and far more significant variable was one concerning sampling. The approach being studied intrinsically depends upon an accurate knowledge of the component composition of a particular asphalt both at the time of initial exposure to the accelerated cycle and at final failure. The evolutionary nature of this study made it necessary to determine component analysis of the asphalts, before weathering, on samples obtained from the five-gallon pails in which they had been stored for three years. These samples were not necessarily representative of those taken for durability studies. It was subsequently shown that the component composition of the surface of these aged asphalts was significantly different than that of the body of the material which was naturally protected from atmospheric influences. In addition, it was shown that the depth to which the various asphalts were affected was not the same. Table 2 illustrates the difference in component composition between the surface and body of five of the asphalts studied.

TABLE 2.

Asphalt	% Asphaltenes Surface	% Asphaltenes Body
Ambit	46.3	38.4
Envoy	44.8	40.6
East Venezuelan	40.6	37.2
Laguinillas	42.9	40.5
Louisiana	43.1	36.5

Since the actual initial composition of the material that was weathered lies somewhere between these two extremes, the scatter of points obtained both above and below the representative curve was expected. In future work, this effect will easily be minimized by making the necessary analysis on a sample poured from the same batch being used to make coatings for accelerated exposures.

6. CONCLUSIONS

For the twenty asphalts employed and within the limits of the variables previously cited, a good correlation appears to exist between the rate of formation of asphaltenes and the accelerated durability of an asphalt.

The rate of change of total oils may similarly and perhaps more rigorously be employed to obtain a similar relationship. However, the former may be used to better advantage since it requires less time to determine and is very reproducible.

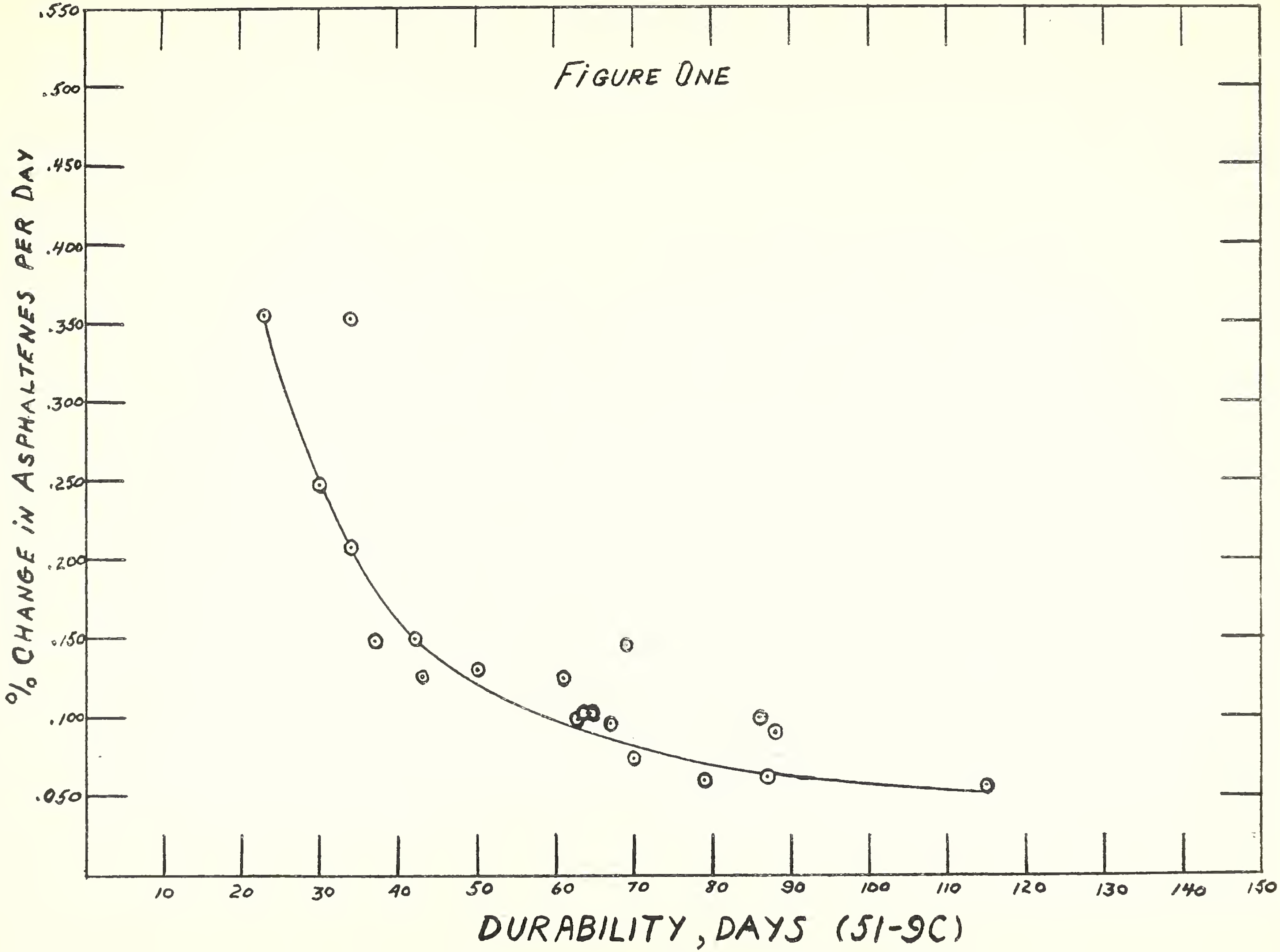
7. REFERENCES

(1) Kleinschmidt, L. R., "Chromatographic Method for the Fractionation of Asphalts Into Distinctive Groups of Components", J. Res. NBS 54, 163-166, 1955.

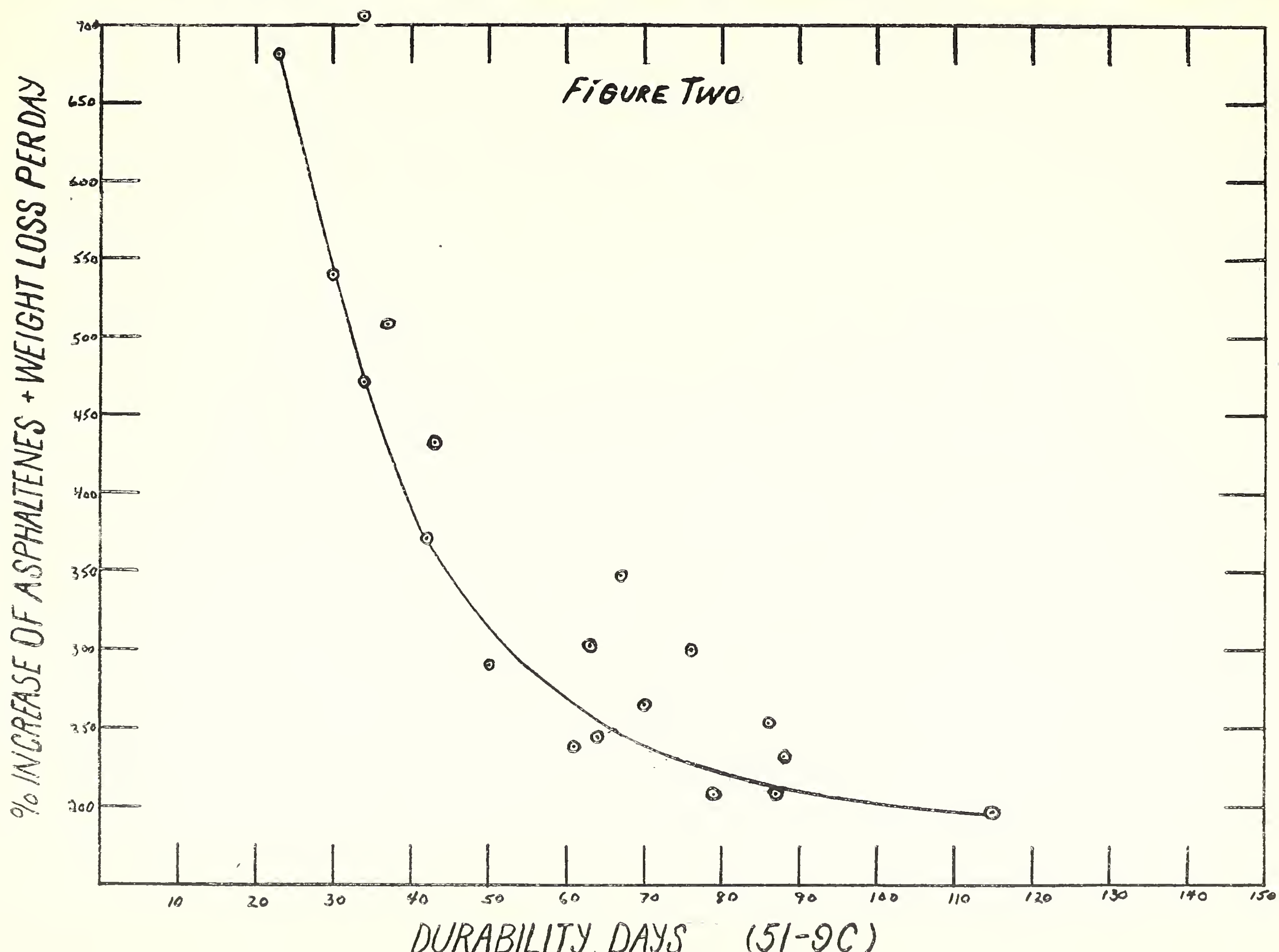
(2) Greenfeld, S. H., "A Method of Preparing Uniform Films of Bituminous Materials, ASTM Bulletin 193, 50-53, October 1953.

(3) Monthly Progress Report No. 108, Asphalt Roofing Industry Bureau, May 8, 1958.

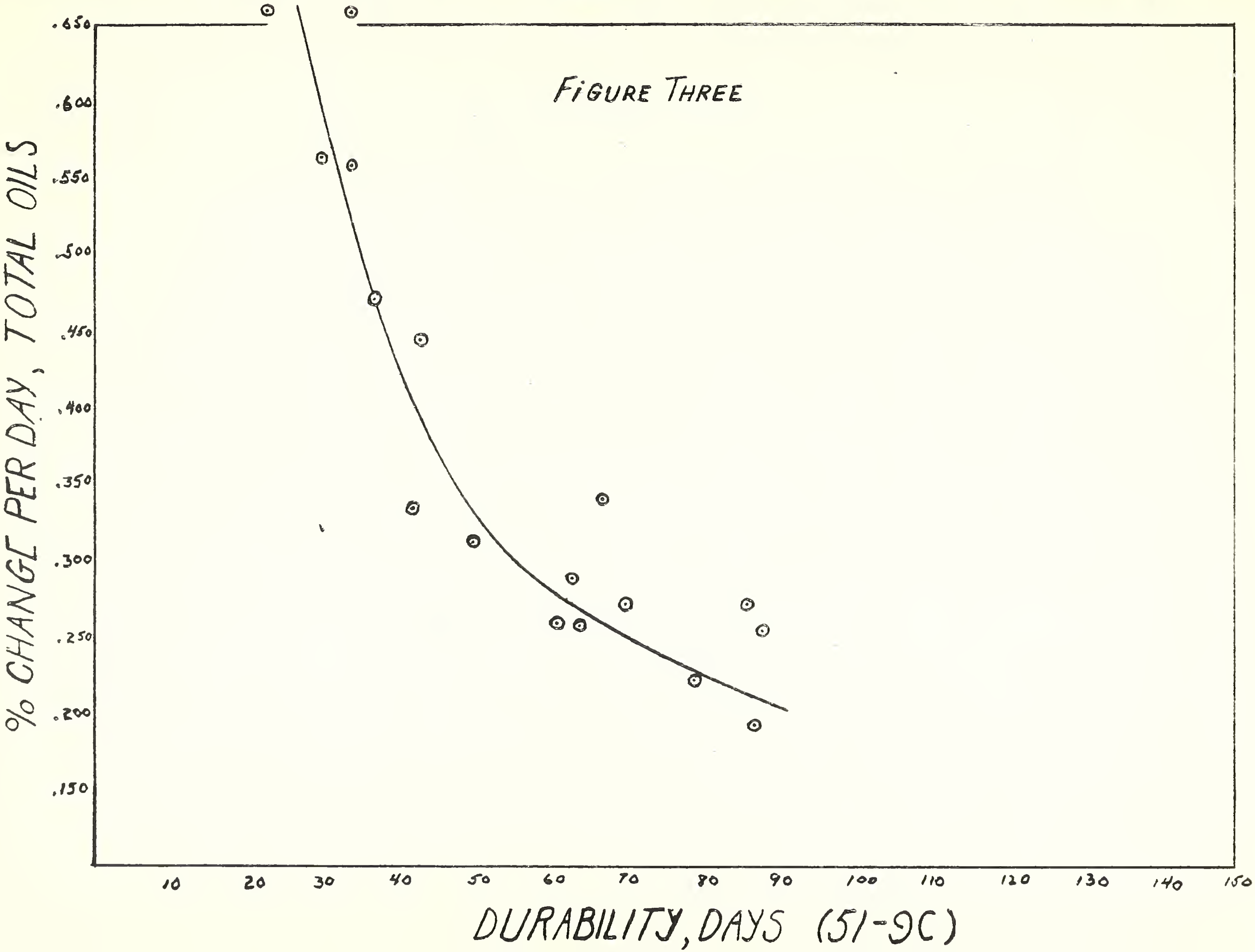
RATE OF FORMATION OF ASPHALTENES VS. ACCEL. DURAB.



RATE OF INCREASE OF ASPHALTENES + WT. LOSS VS. ACCELER. DURABILITY



RATE OF DECREASE OF TOTAL OILS VS. ACCELERATED DURABILITY



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