### ANTIOXIDANTS FOR PAVING ASPHALTS

by

R. N. Traxler Research Engineer Texas Transportation Institute

> Progress Report No. 3 Research Project No. 15

Submitted to Research Committee of the Texas Highway Department

September 1, 1962

Texas Transportation Institute A. & M. College of Texas College Station, Texas

#### ABSTRACT

Report: Progress Report No. 3 — Research Project No. 15

<u>Title:</u> Antioxidants for Paving Asphalts

Period: November 1, 1960 to September 1, 1962

Objectives: Determine how the durability of paving asphalts can be improved.

<u>Experimental</u>: Sixteen chemical additives from two different manufacturers were evaluated as antioxidants for 85-100 penetration paving asphalts. Thin films of the additive-containing asphalts were subjected to oxidation for various times at different temperatures and the viscosities of the hardened material determined in the microfilm (sliding plate) viscometer. The same type of data were obtained on the straight asphalt to determine the protection supplied by the additive.

Conclusions: The following conclusions are drawn from the data given in this report.

- Chemical compounds are available which serve rather effectively as anti-oxidants and free radical inhibitors when added to asphalt cements.
- (2) The retardation of hardening by these chemicals is most effective in asphalts that are highly susceptible to oxidation.
- (3) One to two weight percent of the additive material appears to be the optimum concentration.
- (4) The additives investigated are more effective against oxidation in the absence of light than against the severe hardening caused by photo-oxidation.

<u>Recommendations</u>: It is recommended that publicity be given to the results obtained to date in order to stimulate development and promotion of even more effective additives by the chemical industry.

<u>Future work</u>: The manufacturer of the B series of additives is working toward the development of chemicals that will be even more effective than their additive B-8. When the new products are submitted they will be evaluated in asphalts of interest to the Texas Highway Department.

The Texas Transportation Institute has a contract with the National Bituminous Concrete Association which includes studies on additives that will improve the durability of paving asphalts. Work done under this contract will be coordinated to assure no duplication of the investigations under Research Project No. 15 and to guarantee maximum benefit to each sponsor.

# CONTENTS

Section	Title	<u>e</u>
I.	OBJECTIVES OF RP-15	
II .	HISTORY	
III .	CONCLUSIONS	
IV .	RECOMMENDATIONS	
V.	FUTURE WORK	ł
VI.	EXPERIMENTAL 5	
	<ul> <li>1-Materials Investigated</li> <li>2-Testing Procedure</li> <li>3-Data on Additives No, A</li> <li>4-Screening Tests on Additives No, B</li> <li>5-Preliminary Tests on Additive No, B-8</li> <li>6-Further Tests on Additive No, B-8</li> </ul>	; ; ; ;
VII.	APPENDIX	 F
	Tables	
Number	<u>Title</u> Page	<u>e</u> _
1.	Effect of Additives No. A on Asphalt No. 1 (85-100 Penetration grade)	,
2.	Effect of Additive No. A-2 on Asphalt No. 1 (85-100 Penetration grade) 9	•
3.	Effect of Additive No. B-8 on Asphalt No. 1 (85-100 Penetration grade	
4.	Effect of Additive No. B-8 on Asphalt No. 1 Heated for Short times in Air and Nitrogen	}.
5.	Asphalt No. 1 Heated in the Dark Between Glass Plates for 4 hours at 225-375° F	ŀ
6.	Thin Films Heated in the Dark Between Glass Plates for 4 hours at 325° F and 350° F	5

# CONTENTS (Cont'd)

Number	Figures									Page
1.	Oven Oxidation of 15 Micron Films	•	٠	•	•		•		°	17
2.	Photooxidation of 15 Micron Films	.4.		٠	۵.	*	,•	¢	•	20

### ANTIOXIDANTS FOR PAVING ASPHALTS

### I. OBJECTIVES OF RP-15.

The goals of this project are to:

- (1) Investigate the paving asphalts used by the Texas Highway Department,
- (2) Establish specifications to assure use of superior asphalts by the Department, and
- (3) Determine how the durability of paving asphalts can be improved.

#### II. HISTORY

Research Project 15, "Modifications of Properties of Asphalt", was initiated February 1, 1959. Work on Objective No. 3 was started November 1, 1960.

Additives are rather widely used in asphalt to improve adhesion to damp aggregates and other solid surfaces and to retard stripping from solid surfaces. A number of companies are involved in the manufacture of antistripping compounds. However, little research has been done to develop additives which will reduce the susceptibility of paving asphalts to hardening by oxygen and sunlight at reasonably high temperatures.

In conversations with two chemical companies it was determined that they could supply chemicals that might serve as free radical inhibitors and reducing agents. Since such materials should increase the resistance of asphalt cements to hardening by heat, oxygen, and sunlight arrangements were made to investigate the different materials offered.

#### III. CONCLUSIONS

The following conclusions are drawn from the data given in this report.

- Chemical compounds are available which serve rather effectively as antioxidants and free radical inhibitors when added to asphalt paving cements.
- 2. The retardation of hardening by these chemicals is most effective in asphalts which are highly susceptible to oxidation.
- 3. One to two percent of the additive material appears to be the optimum concentration.
- 4. The additives investigated are more effective against oxidation in the absence of light than against the severe hardening caused by photooxidation.

#### IV. RECOMMENDATIONS

It is recommended that publicity be given to the results obtained to date in order to stimulate development and promotion of even more effective additives by the chemical industry.

#### V. FUTURE WORK

The manufacturer of the B series of additives is working toward the development of chemicals that will be more effective than their additive B-8. When the new products are submitted they will be evaluated in asphalts of interest to the Texas Highway Department.

The Texas Transportation Institute has a contract with the National Bituminous Concrete Association which includes studies on additives that

will improve the durability of paving asphalts. Work done under this contract will be coordinated to assure no duplication of the investigations under Research Project No. 15 and to guarantee maximum benefit to each sponsor.

### VI. EXPERIMENTAL

### 1. Materials Investigated

The chemicals investigated came from two sources:

- (a) Company A supplied additives No.'s A-1, A-2 and A-3. Company B submitted additives No.'s B-1 thru B-13.
- (b) Three 85-100 penetration asphalts supplied by the Texas Highway Department were used to evaluate the effectiveness of the 16 different additives. These were:

Asphalt No. 1 which is highly susceptible to oxidation.

Asphalt No. 11 which is moderately susceptible to oxidation.

Asphalt No. 6 which is highly resistant to oxidation.

Properties of these asphalts are given in Progress Report No. 1

of Research Project 15, dated February 1, 1961.

### 2. Testing Procedure

A weighed amount (up to 3%) of the additive was thoroughly blended with the selected 85-100 penetration grade asphalt. Care was taken that the mixture was not overheated. The microfilm viscometer was used to determine the viscosities of the blends at 77° or 95° F. The viscosities were calculated at 5 x  $10^{-2}$  sec.<sup>-1</sup>, and in some of the experiments also at a power input of 1000 ergs/sec./cm<sup>3</sup>.

Next, a 15-micron film of the blend was placed on a 4 by 4 cm glass plate and exposed to heat, air, and sunlight at various temperatures for different times. The hardened asphalt was scraped from the glass surface and placed between 2 by 3 cm plates used in the microfilm viscometer. The viscosities of the treated blends were determined at the temperature used for evaluating the original, untreated blend. The viscosity of the hardened blend was divided by that of the original untreated blend to obtain the Relative Viscosity of the treated material. This value was compared with the R.V. of the original asphalt exposed to the same environment to determine the effect of the additive. If the R,V. of the treated blend was significantly less than that of the treated original asphalt, the additive was considered to be worthy of further consideration.

# Table 1

## Effect of Company A Additives on Asphalt No. 1, 85-100 Penetration Grade

			15-Mi	cron Films	Heated in A		an gan an a	
		250°F	•		Min Warr of a management of Min Cambor strategy and	<u>275°</u>	F	
		L <u>.</u>		<b>1.</b>			30 min	•
Viscosity Poises @ 77	Poises @77°F	R.V.	1	R.V.	Poises @77°F			R.V
1.10 x 10 <sup>6</sup>	$2.3 \times 10^{6}$	2.1	$4.0 \times 10^{6}$	3.6	3.5 × 10 <sup>6</sup>	.2	$6.6 \times 10^{6}$	6.0
$0.8 \times 10^6$	$1.7 \times 10^{6}$	2.1	$3.0 \times 10^{6}$	3.75	$2.2 \times 10^{6}$	• 8	5.7 x 10 <sup>6</sup>	7.1
$0.8 \times 10^{6}$	$1.8 \times 10^{6}$	2.25	$3.5 \times 10^{6}$	4.4	$2.2 \times 10^{6}$	• 8	5.4 x $10^{6}$	6.6
$1.4 \times 10^{6}$	$3.1 \times 10^{6}$	2.2	$3.9 \times 10^{6}$	2.8	$3.4 \times 10^{6}$	. 4	7.6 x 10 <sup>6</sup>	5.4
	$1.10 \times 10^{6}$ $0.8 \times 10^{6}$ $0.8 \times 10^{6}$	Viscosity       Poises         Poises @ 77       @77°F         1.10 x 10 <sup>6</sup> 2.3 x 10 <sup>6</sup> 0.8 x 10 <sup>6</sup> 1.7 x 10 <sup>6</sup> 0.8 x 10 <sup>6</sup> 1.8 x 10 <sup>6</sup>	15 min.Viscosity PoisesPoises $@77$ Poises $@77^{\circ}F$ R.V.1.10 x 10^62.3 x 10^62.10.8 x 10^61.7 x 10^62.10.8 x 10^61.8 x 10^62.25	$\begin{array}{c cccc} & & \frac{15 \text{ min.}}{\text{Poises}} & \frac{30 \text{ mir}}{\text{Poises}} \\ \hline & & 15 \text{ min.} & \frac{30 \text{ mir}}{\text{Poises}} \\ \hline & & \text{Poises} & 0.77 & 0.79 & \text{R.V.} & 0.77 & \text{Poises} \\ \hline & & 0.10 \times 10^6 & 2.3 \times 10^6 & 2.1 & 4.0 \times 10^6 \\ \hline & & 0.8 \times 10^6 & 1.7 \times 10^6 & 2.1 & 3.0 \times 10^6 \\ \hline & & 0.8 \times 10^6 & 1.8 \times 10^6 & 2.25 & 3.5 \times 10^6 \end{array}$	$250^{\circ}F$ Viscosity Poises15 min. Poises @77 $\odot$ R.V.30 min. Poises @77^{\circ}F R.V.1.10 x 10^62.3 x 10^62.1 $4.0 \times 10^6$ 1.10 x 10^62.3 x 10^62.1 $4.0 \times 10^6$ $3.6$ 0.8 x 10^61.7 x 10^62.1 $3.0 \times 10^6$ $3.75$ 0.8 x 10^61.8 x 10^6 $2.25$ $3.5 \times 10^6$ $4.4$	Viscosity Poises15 min. Poises30 min. Poises15 min. Poises @77°F1.10 x 10^62.3 x 10^62.1 $4.0 \times 10^6$ $3.6$ $3.5 \times 10^6$ 0.8 x 10^61.7 x 10^62.1 $3.0 \times 10^6$ $3.75$ $2.2 \times 10^6$ 0.8 x 10^61.8 x 10^6 $2.25$ $3.5 \times 10^6$ $4.4$ $2.2 \times 10^6$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	250°F275°F15 min.30 min.15 min.ViscosityPoises90 min.PoisesPoises90 min.

#### 3. Data on Additives No. A

Two percent of each of the three additives submitted by Company A were incorporated in Asphalt No. 1 which possesses rather high susceptibility to hardening by air (oxygen) and heat. The original asphalt and

the heated and unheated asphalt and biends were determined in the microfilm viscometer. The viscosities of the heated samples were divided by the viscosities of the unheated materials to obtain the relative viscosity (R.V.) of each material. Table 1, facing, shows the data obtained. In general 2% Additives No. A-1 and No. A-3 were not effective in reducing the tendency of Asphalt No. 1 to harden under the conditions employed. Under certain conditions of time and temperature 2% of No. A-2 effected some improvement.

In additional experiments 2% blends of No. A-2 were heated for 60 minutes in air and nitrogen at  $275^{\circ}$  and  $300^{\circ}$  F and viscosities determined. Data are given in <u>Table 2</u> following. At  $275^{\circ}$  and  $300^{\circ}$  F 2% of No. A-2 reduced the susceptibility of Asphalt No. 1 to hardening by heat and air by about 50 percent. The effect in an atmosphere of nitrogen was negligible.

Films of Asphalt No. 1 and the blend of 2% No. A-2 in Asphalt No. 1 were next heated between glass plates in the dark at  $325^{\circ}$  for 4 hours. Under these conditions Asphalt No. 1 shows sufficient condensation polymerization to give a R.V. of 3.8. The blend gave a R.V. of 1.40 indicating that the additive retards this type of hardening to some extent.

## Table 2

\*

¥

## Effect of Additive No. A-2 on Asphalt No. 1, 85-100 Penetration Grade

	15-Micron F	<mark>ilms Heate</mark>	d for 60 Minu	<u>3 @ 275°F</u>
	In Air		In	trogen
Viscosity Poises @ 77°F	Poises @ 77°F	R.V.	Poises @ :	F R.V.
$1.1 \times 10^{6}$	$12.5 \times 10^{6}$	11.4	3.0 x 16	2.7
$1.4 \times 10^{6}$	$8.8 \times 10^{6}$	6.3	4.5 x 10	3.2
	15-Micron	ed for 60 Minı	s@300°F	
	In Air	••• • • •	In	itrogen
Poises @ 77°F	Poises @ 77°F	R.V.	Poises @	°F R.V.
$1.1 \times 10^{6}$	$21.0 \times 10^{6}$	19.1	3.0 x 10	2.7
$1.4 \times 10^{6}$	$12 \times 10^{6}$	8.6	3.9 x 1(	2.8
	Poises @ 77°F 1.1 x 10 <sup>6</sup> 1.4 x 10 <sup>6</sup> Poises @ 77°F 1.1 x 10 <sup>6</sup>	In AirViscosity Poises @ 77°FPoises @ 77°F $1.1 \times 10^6$ $12.5 \times 10^6$ $1.4 \times 10^6$ $8.8 \times 10^6$ $15-Micron$ $15-Micron$ In AirIn AirPoises @ 77°FPoises @ 77°F $1.1 \times 10^6$ $21.0 \times 10^6$		Viscosity Poises @ 77°F       Poises @ 77°F       R.V.       Poises @ : $1.1 \times 10^6$ $12.5 \times 10^6$ $11.4$ $3.0 \times 16$ $1.4 \times 10^6$ $8.8 \times 10^6$ $6.3$ $4.5 \times 10$ $15-Micron Films Heated for 60 Mint       15-Micron Films Heated for 60 Mint         In Air       In         Poises @ 77°F       Poises @ 77°F         1.1 \times 10^6 21.0 \times 10^6 19.1 3.0 \times 10^6 19.1 3.0 \times 10^6 $

**`**\$

#### 4. Screening Tests on Company B Additives

Sample No. B-1 when added to Asphalt No. 1 produced a blend which would not adhere to a glass plate. However, the remaining 12 materials submitted by Company B were screened by preparing 1% blends of each additive in Asphalt No. 1 and subjecting 15-micron films to oxidation in the dark at 250°, 275° and 300° F for 15 and 30 minutes. Only blends of B-6, B-7, B-8, and B-9 were tested for 30 minutes at 300° F. Viscosities of all of the blends before and after oxidation were measured in the microfilm viscometer at 77° F. The R.V. of each hardened material was determined and compared with that of Asphalt No. 1 treated in the same manner. <u>Table A-1</u> in the Appendix, gives the data obtained. It was concluded that additive No. B-8 offered the greatest promise as an antioxidant. Field tests by Company B have indicated that this material also is promising as an adhesion additive. The decision was made to limit further investigations to blends made with No. B-8.

# Table 3

### Effect of Additive B-8 on Asphalt No. 1, 85-100 Penetration Grade

		15-Micron Films Heated for 60 Minute							
		In Air		In	trogen				
Sample	Poises @ 77°F	Poises @ 77°F	R.V.	Poises @ <sup>c</sup>	R <sub>∘</sub> V.				
Asphalt No. 1	$1.1 \times 10^{6}$	$12.5 \times 10^{6}$	11.4	$3.0 \times 10^{-1}$	2.7				
No. 1 + 1% B-8	$1.1 \times 10^{6}$	$4.0 \times 10^{6}$	3.6	3.1 x 1(	2.8				

	Τ				
	In Air		In	trogen	n
<u>s @ 77°F</u>	Poises @ 77°F	R.V.	Poises @	°F	R.V.
106	$21.0 \times 10^{6}$	19.1	$3.0 \times 10^{6}$		2.7
10 <sup>6</sup>	$7.5 \times 10^{6}$	6.8	$2.5 \times 10^{6}$		2.3
	<u>s @ 77°F</u> 10 <sup>6</sup> 10 <sup>6</sup>	$21.0 \times 10^6$	$10^{6}$ 21.0 x 10 <sup>6</sup> 19.1	$10^{6}$ 21.0 x 10 <sup>6</sup> 19.1 3.0 x 10 <sup>6</sup>	$10^{6}$ 21.0 x 10 <sup>6</sup> 19.1 3.0 x 10 <sup>6</sup>

### 5. Preliminary Tests on Additive No. B-8

<u>Oxidation and Volatilization</u>: A blend of 1% B=8 in Asphalt No. 1 was heated (in the form of 15-micron films) in air (oxygen) and nitrogen for 60 minutes at 275° and 300° F. Viscosities of the untreated and of the hardened materials were determined and relative viscosities calculated in the usual manner. <u>Table 3</u>, facing, shows the data obtained. It is evident that, under this protracted heating at high temperatures, 1% of the additive reduces the hardening to about one-third of the hardening experienced by the original Asphalt No. 1. Again, the additive had no appreciable effect on volatilization.

Similar experiments were performed at  $275^{\circ}$  F for 15 and 30 minutes. As would be expected, the results of the treatment at these shorter periods of time were not as exaggerated as shown in Table 3 where the exposure time was 60 minutes. Data for 15 and 30 minutes heating in air and nitrogen at  $275^{\circ}$  F are given in <u>Table 4</u>, following. Again 1% of B-8 appears to materially reduce the oxidation of Asphalt No. 1. It is pointed out that the data obtained after 15 and 30 minutes heating are not as accurate as those shown for the 60-minute tests. This condition arises because of difficulty in attaining a temperature of  $275^{\circ}$  F for the full 15- or 30-minute period.

# Table 4

4

r

×.

÷.

where we shall be seen in the second

×.

## Effect of Additive B-8 on Asphalt No. 1 Heated for Short Times in Air and Nitrogen

	15-Micron F	ilm Heated f	@ 275°F		
	In Air		I	Nitroge	<u>n</u>
Poises @ 77 <sup>6</sup> F	Poises @ 77°F	R.V.	Poises (	<u>'7°F</u>	R.V
$1.1 \times 10^{6}$	$3.5 \times 10^{6}$	3.2	1.7 x	6	1.5
$1.1 \times 10^{6}$	$1.9 \times 10^{6}$	1.8	1.4 x	6	1.3
	15-Micron F	ilm Heated f	or 30 Minute	<u>@ 275°</u>	F
	In Air		<u>Ir</u>	Jitroger	1
Poises @ 77°F	Poises @ 77°F	R.V.	Poises	77°F	R.V
$1.1 \times 10^{6}$	$6.6 \times 10^{6}$	6.00	2.2 x	6	2.0
$1.1 \times 10^{6}$	$5.0 \times 10^{6}$	4.55	1.8 x	6	1.6
	$1.1 \times 10^{6}$ $1.1 \times 10^{6}$ <u>Poises @ 77°F</u> $1.1 \times 10^{6}$	In Air           Poises @ 77°F         Poises @ 77°F $1.1 \times 10^6$ $3.5 \times 10^6$ $1.1 \times 10^6$ $1.9 \times 10^6$ $1.1 \times 10^6$ $1.9 \times 10^6$ In Air         In Air           Poises @ 77°F         Poises @ 77°F $1.1 \times 10^6$ $6.6 \times 10^6$	In Air           Poises @ 77°F         Poises @ 77°F         R.V. $1.1 \times 10^6$ $3.5 \times 10^6$ $3.2$ $1.1 \times 10^6$ $1.9 \times 10^6$ $1.8$ $1.1 \times 10^6$ $1.9 \times 10^6$ $1.8$ $15$ -Micron Film Heated f         In Air           Poises @ 77°F         Poises @ 77°F         R.V. $1.1 \times 10^6$ $6.6 \times 10^6$ $6.00$	Poises @ 77 <sup>b</sup> F         Poises @ 77 <sup>o</sup> F         R.V.         Poises () $1.1 \times 10^6$ $3.5 \times 10^6$ $3.2$ $1.7 \times$ $1.1 \times 10^6$ $1.9 \times 10^6$ $1.8$ $1.4 \times$ $15-Micron Film$ Heated for 30 Minute         In Air         Ir           Poises @ 77 <sup>o</sup> F         Poises @ 77 <sup>o</sup> F         R.V.         Poises () $1.1 \times 10^6$ $6.6 \times 10^6$ $6.00$ $2.2 \times$	In AirINitrogePoises @ 77°FPoises @ 77°FR.V.Poises @ '7°F $1.1 \times 10^6$ $3.5 \times 10^6$ $3.2$ $1.7 \times 6$ $1.1 \times 10^6$ $1.9 \times 10^6$ $1.8$ $1.4 \times 6$ $15-Micron Film Heated for 30 Minute@ 275°In AirIrJitrogerPoises @ 77°FPoises @ 77°FR.V.Poises @ 77°FPoises @ 77°F77°F1.1 \times 10^66.6 \times 10^66.002.2 \times 16^6$

.

Table	5

### Asphalt No. 1 Heated in the Dark Between Glass Plates for 4 Hours at 225-375°F

225°F		325°F		350°F	37 5°F		
Poises @ 77°F	<u>R.V.</u>	<u>Poises @ 77°F</u>	<u>R.V.</u>	Poises @ 77°F	<u>R.V.</u>	bises @ 77°F	<u>R.V.</u>
$1.3 \times 10^{6}$	1.2	$4.2 \times 10^{6}$	3.8	$1.9 \times 10^{6}$	1.70	$1.7 \times 10^{6}$	1.55

<u>Condensation Polymerization</u>: A few experiments were performed to determine the extent Asphalt No. 1 is hardened by heat in the absence of oxygen, light, and volatilization and whether Additive B-8 is able to reduce condensation polymerization. First, 15-micron films of Asphalt No. 1 were placed between glass plates and heated in the dark for 4 hours at 225°, 325°, 350°, and 375°F. The plates were separated, the heated films of asphalt removed and viscosities determined at 77°F. <u>Table 5</u> facing shows that Asphalt No. 1 increases in viscosity when heated from 225° to 325°F. At 350° F the R.V. value decreases sharply indicating that at this high temperature the asphalt depolymerizes or cracks which decreases the viscosity. At 375°F the depolymerization is even more exaggerated. Cracking is visibly evident by the presence of carbonaceous particles and gas bubbles in the highly heated films.

Films of the blend of 1% B-8 in Asphalt No. 1 were heated between plates in the dark at  $325^{\circ}$  and  $350^{\circ}$ F and the resulting relative viscosities compared with those of the straight asphalt. <u>Table 6</u> below shows that 1% of B-8 definitely decreases the amount of hardening caused by heat alone at  $325^{\circ}$ F. At  $350^{\circ}$ F the additive does not affect the course of the depolymerization reaction.

#### Table 6

Thin Films Heated in the Dark Between Glass Plates for 4 Hours at  $325^{\circ}$  and  $350^{\circ}$  F

	325° F		350°F				
Sample	Poises @ $77^{\circ}F$	R.V.	Poises @ 77°F	R.V.			
Asphalt No. 1	$4.2 \times 10^{6}$	3.8	$1.9 \times 10^{6}$	1.7			
No. 1 + 1% B-8	$1.7 \times 10^{6}$	1.55	$1.9 \times 10^{6}$	1.7			

#### 6. Further Tests on Additive B-8

Oxidation for 60 Minutes: One part of additive B-8 was blended with 99 parts of Asphalt No. 1 and Asphalt No. 11 respectively. Asphalt No. 6 which is highly resistant to oxidation was used as a reference material. Films of the original asphalts and of the blends were heated in an air oven for 60 minutes at 200°, 250°, and 300° F. Viscosities of the original asphalts and the hardened films were determined in the microfilm viscometer at 95° F and relative viscosities calculated. Data calculated for a rate of shear of  $5 \times 10^{-2}$  reciprocal seconds are given in Table A-2. Table A-3 in the Appendix gives the viscosities of the same materials calculated at a power input of 1000 ergs/sec/cm<sup>3</sup>.

At a temperature of 200° F, 1% of additive B-8 does not appreciably retard the hardening of either Asphalts No. 1 or No. 11 as measured by the relative viscosity. At 250° F the additive has little effect on Asphalt No. 11 but reduces the susceptibility of Asphalt No. 1 to oxidation. When the 15-micron films were heated for 60 minutes at 300° F the oxidation of both Asphalts 1 and 11 are markedly retarded by B-8. However, the effect is greater with Asphalt No. 1 than with No. 11. The presence of 1% of the additive did not reduce the susceptibility of either asphalt enough to make them as resistant as Asphalt No. 6 which is an exceptionally resistant material. However, 1% of additive makes Asphalt No. 1 about as resistant as Asphalt No. 11. The latter asphalt without additive shows average resistance to oxidation.



Figure I, facing, is a semilog plot of pertinent data which indicate the relative susceptibilities of Asphalts No. 1, 6, and 11 to oxidation at high temperatures. Asphalt No. 1 containing 1% of B-8 has essentially the same resistance to oxidation or Asphalt No. 11. <u>Photooxidation at 190° F</u>: This temperature was easy to attain and regulate in the apparatus used. Fifteen micron films of the original asphalts and blends were exposed to radiation from a 175-watt Mazda Sunlamp for 1, 2 and 3 hours. Viscosities were measured at 95° F and relative viscosities calculated as described above. Table A-4 of the Appendix gives the data calculated at a rate of sheat of  $5 \times 10^{-2}$  reciprocal seconds. Table A-5 gives the viscosities of the same materials calculated at a power input of 1000 ergs/sec/cm<sup>3</sup>. The hardening by photooxidation is much more severe than by oxidation in the dark.

In the 1-hour tests, 1% of B-8 had no appreciable effect on Asphalt No. 11, but with Asphalt No. 1 the relative viscosity dropped from 6.2 for the straight asphalt to 4.7 for the blend.

For 2 hours exposure 1% additive had little effect on Asphalt No. 11 but the additive in Asphalt No. 1 caused a considerable reduction (12.4 to 10.0) in relative viscosity. When 2% B-8 was used in Asphalt No. 1 heating at 190° F for 2 hours reduced the relative viscosity from 12.4 to 7.6. A blend containing 3% of additive when exposed for 2 hours at 190° F resulted in a reduction of R.V. from 12.4 to 9.2. Thus 2% of B-8 appears to be the optimum amount in Asphalt No. 1 for retarding photooxidation at this time and temperature.

When the blends of Asphalts No. 11 and 1 with 1% B-8 were exposed for 3 hours at  $190^{\circ}$  F the effect on Asphalt No. 11 was slight but the additive reduced the R.V. of Asphalt No. 1 from 30 to 20.



Figure II, facing, is a semilog plot of the significant data concerning the effect of photooxidation on Asphalts No. 1, 6 and 11. The addition of 1% B-8 considerably reduces the susceptibility of Asphalt No. 1 to photooxidation but the blend does not approach Asphalt 11 in resistance. Additive B-8 is not as effective in retarding the hardening caused by photooxidation as it is for straight oxidation.

### VII. APPENDIX

Index

<u>Table</u>	Title	Page
A-1	Effect of B Additives on Asphalt No. 1, 85-100 penetration grade	23
A-2	Oven Oxidation for 60 minutes — 15-Micron Films — $5 \ge 10^{-2} \text{ sec.}^{-1}$	24
A-3	Oven Oxidation for 60 minutes — 15-Micron Films — 1000 ergs/sec/cm <sup>3</sup>	25
A-4	Photooxidation at $190^{\circ}F - 15$ -Micron Films - $5 \times 10^{-2}$ sec1	26
A- 5	Photooxidation at 190°F — 15-Micron Films — 1000 ergs/sec/cm <sup>3</sup>	27

ie.

r

÷

### Effect of B Additives on Asphalt No. 1, 85-100 Penetration Grade

							15-Micr	on Film	s Heated in	Air				
				2	50°F		1	27	′5°F			300	°F	
			<u> </u>	n	30 Mir	1.	15 Mir	1.	30 Mir	1.	15 Mi		30 M	in.
. <u>.</u>	Sample	Poises @77°F	Poises @ 77°F	R.V.	Poises @77°F	R.V.	Poises @ 77°F	R.V.	Poises @ 77°F	R.V.	Poises @ 77°F	<u>.V.</u>	Poises @ 77°F	R.V.
	Asphalt No. 1	1.1x10 <sup>6</sup>	2.3x106	2.1	4.0x10 <sup>6</sup>	3.6	3.5x106	3.2	6.6x106	6.0	5.5x106	.0	12x106	10.9
	No.1+2% B-2 No.1+1%	0.95x10 <sup>6</sup>	ν.	2.0	3.6x10 <sup>6</sup>	3.8	3.1x10 <sup>6</sup>	3.5	5.6x10 <sup>6</sup>	5.9	-		-	-
	B-3 No.1+1%	$1.0 \times 10^{6}$	1.8x10 <sup>6</sup>	1.8	$3.3 \times 10^{6}$	3.3	2.7x10 <sup>6</sup>	2.7	$5.4 \times 10^{6}$	5.4	<b>—</b> , ,	-	-	-
	B-4	1.0x10 <sup>6</sup>	1.5x106	1.5	$3.0 \times 10^{6}$	3.0	2.7x106	2.7	4.8x10 <sup>6</sup>	4.8	_	-	-	-
	No.1+1% B-5 No.1+1%	1.1x10 <sup>6</sup>	2.1x10 <sup>6</sup>	1.9	3.5x10 <sup>6</sup>	3.2	3.0x10 <sup>6</sup>	2.7	5.4x10 <sup>6</sup>	4.9	_	-	• • • • •	-
	B-6* No.1+1%	0.8x10 <sup>6</sup>	1.3x10 <sup>6</sup>	1.6	2.1x10 <sup>6</sup>	2.6	1.7x10 <sup>6</sup>	2.2	3.1x10 <sup>6</sup>	3.8	3.5x10 <sup>6</sup>	.3	6.0x10 <sup>6</sup>	7.3
	B-7 No.1+1%	1.1x10 <sup>6</sup>	1.45x106	1.3	2.8x10 <sup>6</sup>	2.5	2.1x10 <sup>6</sup>	1.9	5.4x10 <sup>6</sup>	4.9	5.5x10 <sup>6</sup>	.0	9.5x10 <sup>6</sup>	8.6
	B 8	1.1x106	1.75x106	1.6	2.5x106	2.3	1.9x10 <sup>6</sup>	1.8	5.0x106	4.55	3.6x106	.3	7.4x106	6.7
	No.1+1% B-9 No.1+1%	1.1x10 <sup>6</sup>	1.3x10 <sup>6</sup>	1.2	3.1x10 <sup>6</sup>	2.8	2.6x10 <sup>6</sup>	2.4	6.4x10 <sup>6</sup>	5.8	5.0x10 <sup>6</sup>	• 5	9.5x10 <sup>6</sup>	8.6
	B-10 No.1+1%	0.95x106	1.78x106	1.87	2.16x10 <sup>6</sup>	2.28	2.22x106	2.34	5.56x10 <sup>6</sup>	5.8	3.75x106	.95	-	-
ì	B-11	1.3x106	2.16x106	1.69	3.15x106	2.46	3.28x10 <sup>6</sup>	2.56	6.54x10 <sup>6</sup>	5.1	4.19x10 <sup>6</sup>	.26	- -	-
	No.1+1% B-12	1.2x10 <sup>6</sup>	1.79x10 <sup>6</sup>	1.54	3.06x10 <sup>6</sup>	2.64	2.44x10 <sup>6</sup>	2.10	7.65×10 <sup>6</sup>	6.6	4.31x10 <sup>6</sup>	.70	- -	. —
	No.1+1% B-13	0.95x10 <sup>6</sup>	2.00x10 <sup>6</sup>	2.1	3.47x10 <sup>6</sup>	3.65	2.88x10 <sup>6</sup>	3.04	8.27x10 <sup>6</sup>	8,7	4.96x10 <sup>6</sup>	.22	, - ·	_

\* Has a tendency to draw away from the glass plate when heated.

¥

¢

## Oven Oxidation for 60 Minutes 15-Micron Films 5x10-2sec-1

- 18

•	Original Viscosity	Heated @ 200° F		Heated @ 250° F		Heated @ 300° F	
	Poises @ 95°F	Poises	•:	Poises		Poises	
<u>Asphalt</u>	Shear Rate 5x10-2sec-1	@ <b>9</b> 5°F	R.V.	@ 95°F	R.V.	@ 95°F	R.V.
		- -		. <del>-</del>			
No. 6	$8.4 \times 10^4$	$1.2 \times 10^{5}$	1.4	$1.6 \times 10^5$	1.9	$2.9 \times 10^5$	3.3
No. 11	$1.4 \times 10^5$	$2.4 \times 10^{5}$	1.7	$4.2 \times 10^{5}$	3.0	$1.5 \times 10^{6}$	10.7
No. 11 + 1% B-		$2.3 \times 10^5$	1.75	$4.2 \times 10^5$	3.4	$1.15 \times 10^{6}$	8.9
No. 1	$1.32 \times 105$	$2.6 \times 10^{5}$	2.0	$5.4 \times 10^{5}$	4.1	$2.4 \times 10^{6}$	18.0
No. 1 + 1% B-8	$1.20 \times 10^5$	$2.4 \times 10^{5}$	2.0	$3.6 \times 10^5$	3.0	$1.3 \times 10^{6}$	10.8

9

### Oven Oxidation for 60 Minutes 15-Micron Films Power Input of 1000 ergs/sec/cm<sup>3</sup>

Asphalt	Original Viscosity	Heated at 200°F		<u>Heated at 250°F</u>		Heated @ 300°F	
	Poises @ 95°F 1000 ergs/sec/cm <sup>3</sup>	Poises @ 95°F	R.V.	Poises @ 95°F	R.V.	Poises @ 95°F	R.V.
No. 6	$7.1 \times 10^4$	$1.05 \times 10^{5}$	1.5	$1.5 \times 10^{5}$	2.1	2.7 x $10^5$	3.8
No. 11	$1.2 \times 10^{5}$	$2.1 \times 10^{5}$	1,75	$4.2 \times 10^{5}$	3.5	$1.7 \times 10^{6}$	14.2
No. 11 + 1% B-8	$1.13 \times 10^{5}$	$2.0 \times 10^{5}$	1.75	$4.5 \times 10^5$	4.0	$1.4 \times 10^{6}$	12.5
No. 1	$1.15 \times 10^5$	$2.4 \times 10^{5}$	2.1	5.6 $\times 10^{5}$	4.9	$3.0 \times 10^{6}$	27.0
No. 1 + 1% B-8	$1.05 \times 10^5$	$2.2 \times 10^{5}$	2.1	$3.7 \times 10^5$	3.5	$1.55 \times 10^{6}$	14.8

୍ଦ

\$

# Photooxidation at 190°F 15-Micron Films 5 x 10<sup>-2</sup>sec<sup>-1</sup>

·							
(	Original Viscosity	Exposed 1 hour		Exposed 2 hour		Exposed 3 hours	
Asphalt She	Poises @ 95°F ar Rate 5x10 <sup>-2</sup> sec <sup>-1</sup>	Poises @ 95°F	R.V.	Poises @ 95°F	R.V.	Poises @ 95°F	R.V.
No. 6	$8.4 \times 10^4$	$2.0 \times 10^{5}$	2.4	$2.6 \times 10^{5}$	3.1	$4_{\circ}4 \ge 10^{5}$	5,3
No. 11 No. 11 ± 1% B-8	$1.4 \times 10^{5}$ $1.3 \times 10^{5}$	$4_{*}0 \ge 10^{5}$ $4_{*}0 \ge 10^{5}$	2,9 3.0	9.6 x 10 <sup>5</sup> 7.8 x 10 <sup>5</sup>	6.7 6.0	1,5 x 10 <sup>6</sup> 1,3 x 10 <sup>6</sup>	10.7 10.0
No. 1 No. 1 + 1% B-8	$1.32 \times 10^5$ $1.20 \times 10^5$	8.2 x 10 <sup>5</sup> 5.6 x 10 <sup>5</sup>	6.2 4.7	$1.64 \times 10^{6}$ $1.2 \times 10^{6}$		4.0 x 10 <sup>6</sup> 2,7 x 10 <sup>6</sup>	30.2 20.5
No. 1 + 2% B-8	$1.0 \times 10^{5}$	بالانت خالق علي فالك بالك والم	prod. and and	$7.6 \times 10^{5}$	7.6	,000 (300 CM) (300, 100 ANA (300 ANA)	ටක්, මැට, බංස හැකු
No. 1 + 3% B-8	$7.0 \ge 10^4$	رسىر بىيىر نىيەر ئېچە چەد ھەد جەد. ھەر	بند مبر	$6.4 \times 10^{5}$	9.2	tand came came came and tangtants cam	- FRIG. 1790, 5940 (1880)

٢

# Photooxidation at 190°F 15-Micron Films Power Input of 1000 ergs/sec/cm<sup>3</sup>

Asphalt	Original Viscosity Poises @ 95°F 1000 ergs/sec/cm <sup>3</sup>	Exposed for Poises @ 95°F	<u>1 hour</u> R.V.	Exposed for Poises @ 95°F	2 ho R.V.	Exposed for Poises @ 95°F	3 hours R.V.
No. 6	$7.1 \times 10^4$	$1.9 \times 10^5$	2.7	$2.4 \times 10^5$	3.4	$4.4 \times 10^5$	6.2
No. 11 No. 11 + 1% B-8	$1.2 \times 10^{5}$ $1.13 \times 10^{5}$	$4.0 \times 10^5$ $4.0 \times 10^5$	3.3 2.8	1.0 x 10 <sup>6</sup> 8.5 x 10 <sup>5</sup>	8.3 7.5	1.8 x 10 <sup>6</sup> 1.45 x 10 <sup>6</sup>	15.5 12.8
No. 1 No. 1 + 1% B-8	$1.15 \times 10^5$ $1.05 \times 10^5$	$8.5 \times 10^5$ $5.6 \times 10^5$	7.4 5.3	$1.6 \times 10^{6}$ $1.28 \times 10^{6}$	13.8 12.2	$3.4 \times 10^{6}$ $3.0 \times 10^{6}$	29.6 26.0
No. 1 + 2% B-8	$7.4 \times 10^4$			$8.0 \times 10^{5}$	10.8		
No. 1 + 3% B-8	5.85 x $10^4$			$6.7 \times 10^5$	11.4		ama) 6000. 0000. 0000.