

# CHARACTERIZATION OF ASPHALT VOLATILITY USING TGA AND IATROSCAN ANALYSES

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Studies of asphalt aging on the rooftop frequently focus on oxidation processes and the changes that accompany oxidation. Relatively little attention has been given to the role of volatilization in the aging of asphaltic roofing materials. The reason for this lack of attention is understandable: Very little weight loss is observed in the standard tests. However, the standard tests were developed not to assess long-term changes in asphaltic roofing products but rather to determine short-term effects that occur in a hot-mix paving plant. Roofing products may be better addressed in a manner that takes into account the unique character of these products and the roofing environment. In this work, thermogravimetric analysis (TGA) and Iatroscan chromatography are employed to study the volatility of certain asphalts and the compositional changes that accompany volatilization. Substantial differences in volatility among asphalts are observed, and it is suggested that asphalt volatility is frequently associated with loss of saturates. Possible implications of these results are discussed.

## KEYWORDS

Aging, asphalt, Iatroscan, roofing, thermogravimetric analysis, volatilization.

## INTRODUCTION

The role of oxidation in the aging process has received considerable attention. For example, excellent techniques have been developed in recent years to determine the hardening susceptibilities of asphalts in closed vessels under increased pressure of oxygen.<sup>1</sup> By comparison, relatively little attention has been given to addressing the question of potential shrinkage of roofing compounds brought about by volatilization of asphalt components. In this work, the question is posed: When an asphalt ages, what role might be played by loss of components that can be cooked off on hot days? In a roofing compound, how much shrinkage might accompany volatile losses? Shrinkage, if it occurred, might promote the development of cracks in some types of products.

In addition to the issue of shrinkage, some of the volatile components would likely function as natural plasticizers, and the loss of such components could lead to embrittlement. The combination of shrinkage and embrittlement, if it occurred, would be expected to play a role in the aging process. This role would supplement the well-known contribution of oxidation to aging.

This basic study is not intended to single out particular

types of roofing products or particular aging patterns for study. That lies beyond the scope of this work. The purpose is to provide tools that can help explore the role that volatility may play in the aging process.

## TEST PROGRAM

The test plan was to begin with a survey of 20 asphalts (including both oxidized and paving grades; cf. Table 1) to determine their volatility losses using standard test methods, and then to alter the test procedures in ways that might accentuate any differences observed among the asphalts. The method of ASTM D 6 was employed for the initial survey. In this test, a 50-gram (0.11-pound) sample of asphalt contained in a 90-mil (3-ounce) ointment can is heated for five hours at a temperature of 163°C (325°F). Weight losses after this treatment are reported in Table 2. The values are very low, ranging from 0.01 to 0.14 percent. However, in this test, the asphalt layer is very thick [approximately 2.5 cm (1 inch)]. Because volatilization of molecules from a surface entails a preliminary step of diffusion of molecules to the surface, the thickness of the layer and the limited time of the test are likely to play a dominant role. Such contributing factors leave questions about volatility itself unanswered.

The use of smaller, thinner samples proved revealing. A test was devised using an ointment can lid in place of the can itself. The same set of 20 asphalts was tested, but now the samples weighed 12 grams (0.42 ounces) and the layer thickness was about 6 mm (¼ inch). This provided test conditions more like the thin film oven test (ASTM D 1754). The results are given in Table 3. Observed weight losses in this case ranged from 0.06 to 0.64 percent. Overall, the data indicate that the approximate four-fold reduction in sample weight, from 50 grams to 12 grams (1.76 to 0.42 ounces), increased the percent weight loss by a factor of about four.

Why did the percent weight loss increase when the sample weight was reduced from 50 grams to 12 grams (1.76 ounces to 0.42 ounces)? A comparison of Table 2 with Table 3 reveals that the actual loss in grams for a 50-gram sample was comparable to the loss in grams for the corresponding 12-gram (0.42-ounce) sample. That is so because both samples had the same surface area. The 50-gram (1.76-ounce) sample was four times as thick, but lost the same quantity of volatiles as the thinner 12-gram (0.42-ounce) sample. The weight lost by the thinner sample represented a larger percentage of the sample weight than the same weight lost by the thicker sample. This behavior suggests that much of the volatilization occurs in a thin layer near the surface.

**Table 1: Description of Asphalts**

Asphalt	Description
1	Midcontinent AC-10
2	West Coast Type III
3	West Coast AC-10
4	West Coast AC-20
5	California AC
6	Canadian AC-20
7	Mideast AC-20
8	Venezuelan AC-20
9	Mixed Canadian/Midcontinent/Wyoming AC
10	Mixed Canadian/Midcontinent Saturant grade
11	Midcontinent AC
12	Alaskan North Slope Type III
13	West Coast Type III
14	Mideast Type III
15	Canadian Type III -
16	Mixed Canadian/Midcontinent Type III
17	Mixed Canadian/Midcontinent/Wyoming Type III
18	Midcontinent Type III
19	Venezuelan AC-20
20	Venezuelan Type III

**Table 2: Asphalt Volatilities Determined According to ASTM D 6: 5 hrs. @ 163°C (325°F), 2.5-cm (1-inch) Layer Thickness, 50.0 g (1.76-ounce) Sample Weight**

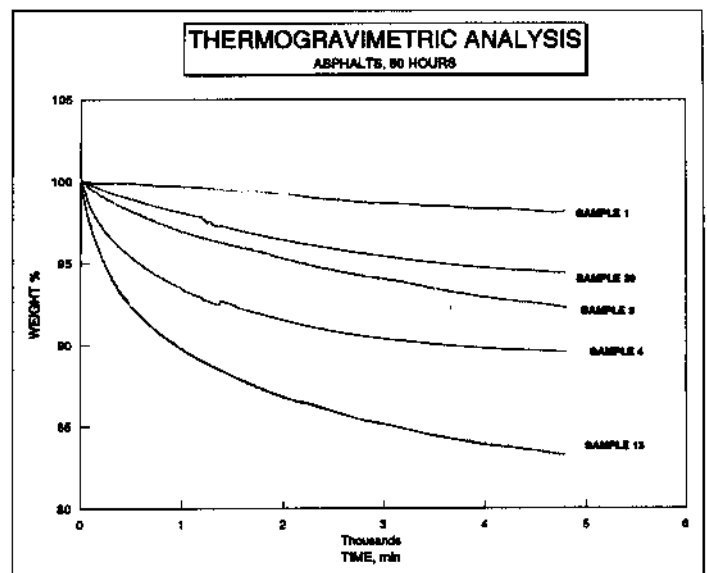
Asphalt	Loss (g)	Loss (%)
1	0.0218	0.04
2	0.0519	0.11
3	0.0687	0.14
4	0.0698	0.14
5	0.0639	0.13
6	0.0285	0.06
7	0.0203	0.04
8	0.0462	0.09
9	0.0391	0.08
10	0.0147	0.03
11	0.0198	0.04
12	0.0188	0.04
13	0.0642	0.13
14	0.0191	0.04
15	0.0111	0.02
16	0.0071	0.01
17	0.0218	0.04
18	0.0129	0.03
19	0.0361	0.07
20	0.0085	0.02

**Table 3: Asphalt Volatilities Determined by Modified ASTM D 6: 5 hrs. @ 163°C (325°F), 6-mm (¼-inch) Layer Thickness, 12.0-g (0.42-ounce) Sample Weight**

Asphalt	Loss (g)	Loss (%)
1	0.0112	0.10
2	0.0492	0.42
3	0.0569	0.48
4	0.0682	0.57
5	0.0552	0.46
6	0.0199	0.17
7	0.0162	0.14
8	0.0464	0.39
9	0.0314	0.27
10	0.0126	0.11
11	0.0089	0.08
12	0.0216	0.18
13	0.0767	0.64
14	0.0211	0.18
15	0.0112	0.09
16	0.0072	0.06
17	0.0218	0.19
18	0.0094	0.08
19	0.0234	0.19
20	0.0081	0.07

**THERMOGRAVIMETRIC ANALYSIS**

The observation that volatilization takes place mostly from a thin surface layer in a short-term test provided the rationale for TGA studies, because this method deals with very small samples [approximately 10 mg (0.00035 ounces), with layer thickness of approximately 0.35 mm (0.014 inches)]. The weight loss of each sample was monitored with a Perkin-Elmer Model



Graph 1.

TGA 7. The test temperature was kept at a constant 163°C (325°F) as in the oven tests. The TGA experiments were done in air. Sample weights were recorded continuously out to 80 hours. Some representative TGA plots are given in Graph 1.

It is evident from the results that volatilization does not stop after five hours, but rather continues throughout the 80-hour experiment. In the authors' sampling of 20 asphalts, weight losses after 80 hours ranged from 1.8 to 17.0 percent. This large range of values helps establish the importance of test conditions in the determination of volatility and serves to underline the wide differences that may be found among various asphalts. It is particularly revealing to find volatility losses as high as 17 percent.

#### THIN LAYER OVEN AGINGS

The TGA experiments were informative but lengthy, because samples are run one at a time. A more rapid survey of volatilities of these asphalts could be performed by oven aging of thin layers. This was done in disposable aluminum weighing dishes with flat bottoms, smooth sides, and flanged rims. Dish diameter was 67 mm (2½ inches). The empty dishes were heated in the oven at 163°C (325°F) overnight and then weighed to four decimal places. Approximately 1.2-gram (0.042-ounce) samples of the 20 asphalts in this survey were weighed to four decimal places, dissolved in tetrahydrofuran, and introduced into the dishes. After evaporation of the solvent at room temperature, the samples were placed in the oven at 163°C (325°F) for aging. The oven was a Blue M Model CC-

09S-F with forced air circulation. Temperatures throughout the oven varied by less than 1°C (2°F). The oven trays were flat, and their levelling was checked with a spirit level.

After five hours, the samples were removed, weight losses were recorded, and the samples were returned to the oven. In this fashion, weight losses were determined after five hours, 20 hours, 40 hours, and 80 hours. Samples were run in triplicate. The results are given in Table 4.

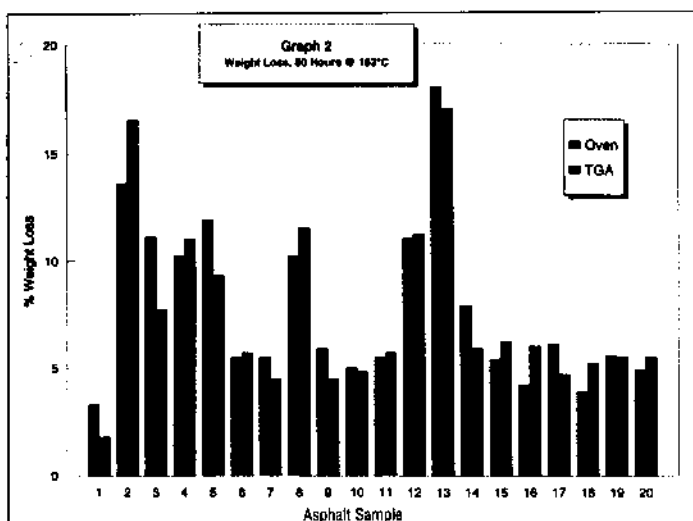
Again, the data show some very large differences in weight loss among the various asphalts. After 80 hours, the largest loss was 18 percent, and the smallest was 3.25 percent. Even after only five hours, there were substantial differences: 5.9 percent for the highest, 0.15 percent for the lowest. The oven data tend to confirm the TGA data. Graph 2 compares TGA and thin layer oven weight loss tests of the 20 asphalts.

#### IATROSCAN CHROMATOGRAPHY

Asphalt is separated into four generic fractions by chromatography. These fractions are the saturates, the naphthene aromatics (or aromatics), the polar aromatics (or resins) and the asphaltenes. The saturates are light-colored oils and consist of saturated hydrocarbons. They are the least-polar constituents of asphalts and would be expected to be more volatile than the other fractions. The naphthene aromatics, polar aromatics, and asphaltenes are progressively darker in color, higher in polarity and less likely to volatilize than the saturates. An outline of the chromatographic fractionation is given in Table 5.

Table 4:  
Asphalt Volatilities Determined by Thin Layer Oven Treatment.  
Samples [1.2 g (0.042 ounces) in 67-mm (2½-inch) dishes] Heated 5 to 80 Hrs. 163°C (@ 325°F).

Asphalt	5 hrs % loss		20 hrs % loss		40 hrs % loss		80 hrs % loss	
	$\bar{x}$	$\sigma$	$\bar{x}$	$\sigma$	$\bar{x}$	$\sigma$	$\bar{x}$	$\sigma$
1	0.21	0.39	0.75	0.44	1.69	0.56	3.26	0.72
2	2.75	0.89	6.74	1.40	10.06	1.83	13.63	2.15
3	2.29	0.71	5.69	1.07	8.62	1.52	11.13	1.75
4	3.01	0.79	5.98	0.94	8.24	1.24	10.17	1.38
5	2.64	0.86	6.30	1.26	9.37	1.69	11.94	1.82
6	0.95	0.23	2.41	0.24	3.82	0.41	5.48	0.62
7	0.63	0.14	2.15	0.25	3.76	0.41	5.47	0.56
8	2.27	0.25	5.62	0.39	8.19	0.66	10.18	0.78
9	0.94	0.26	2.66	0.34	4.12	0.48	5.86	0.60
10	0.43	0.10	1.56	0.14	2.89	0.29	4.98	0.52
11	0.58	0.28	1.98	0.69	3.48	0.69	5.49	0.98
12	1.77	1.10	4.87	2.03	7.53	2.09	11.01	2.13
13	5.92	2.45	11.45	2.51	14.57	2.35	18.02	2.14
14	1.47	0.72	3.88	1.05	5.89	1.12	7.94	1.05
15	0.37	0.29	1.71	0.64	3.22	0.92	5.41	1.22
16	0.15	0.12	1.09	0.19	2.31	0.48	4.23	0.70
17	0.76	0.47	2.34	0.73	3.93	1.05	6.09	1.18
18	0.29	0.22	1.12	0.45	2.25	0.64	3.94	0.77
19	0.62	0.29	2.06	0.43	3.62	0.64	5.58	0.71
20	0.32	0.21	1.61	0.37	3.08	0.62	4.86	0.69



Graph 2.

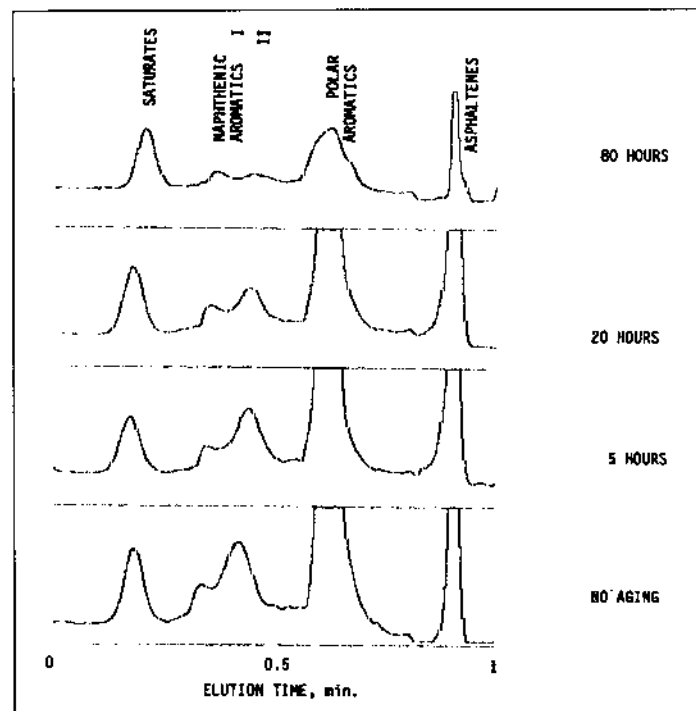
Order of Elution	Fraction	Polarity	Elution Solvent
1	Saturates	Lowest	Heptane
2	Naphthene Aromatics	Low	Toluene
3	Polar Aromatics	Moderate	Tetrahydrofuran
4	Asphaltenes	Highest	(Not eluted)

In Iatroscan chromatography,<sup>2</sup> the separations are performed on very small samples of asphalt applied to a thin layer of finely divided silica adsorbent that is fused to the surface of a quartz rod. This medium is called a Chromarod. To carry out the analysis, first the asphalt is dissolved in a volatile solvent, a drop of the solution is applied near the bottom of the Chromarod, and the solvent is evaporated. Next, the lower part of the rod is immersed in heptane, a solvent that ranks very low in polarity. Capillary action draws the heptane up the rod, past the spot of asphalt. As it migrates, it carries with it the low-polarity constituents of asphalt towards the top of the rod. The heptane is removed from the rod by evaporation, and the process is repeated a second and third time, with progressively stronger solvents. This provides three fractions of asphalt located in separate zones on the rod, plus a fourth fraction that did not migrate but remained at the origin. The amounts of each of these four separated fractions are then determined quantitatively by a flame ionization technique. A hydrogen flame slowly moves along the rod, beginning at one end, burning the constituents of each spot in succession. The combustion produces ions that are collected and detected by a flame ionization detector. The output of the detector can be displayed graphically. The areas under the peaks provide a measure of the amount of each fraction present in the asphalt sample.

Iatroscan chromatography was able to shed light on the events that take place during volatilization in the TGA experiments. The method proved to be well-suited to this purpose because it can handle the very small samples employed in the TGA experiments. Indeed, small sample size proved to be

convenient because the entire specimen could be dissolved in solvent and spotted on the Chromarod. This avoided any problems with representative sampling that might be encountered with larger specimens.

The experimental plan was to run Iatroscan analyses on each asphalt after five hours, 20 hours, and 80 hours in the



Graph 3.

TGA at 163°C (325°F) and to compare these with the initial values on unaged samples. A typical example of Iatroscan curves is given in Graph 3. The data are given in Table 6.

Several trends are clear from the results. Naphthene aromatics and polar aromatics are generally reduced upon prolonged heating. This reduction is very pronounced at 80 hours, but at five hours and 20 hours, the trend is mixed, probably because of stepwise oxidation of naphthene aromatics to polar aromatics to asphaltenes.<sup>5</sup> This stepwise oxidation is portrayed in Scheme 1. The behavior of the asphaltenes is interesting. Initially, the amount of asphaltenes increases because of oxidation of naphthene aromatics and polar aromatics. However, after a longer period, the amount of asphaltenes decreases. This is due to further oxidation of the asphaltenes to insoluble carboids.<sup>4</sup> The carboids, when present, are very evident because they do not dissolve in the solvent employed in spotting the sample on the Chromarod. Because the carboids are not transferred to the rods, the sum of the areas under all the peaks is reduced. This reduction can be very substantial; in many of the samples, after 80 hours, the total peak area was less than 30 percent of their initial values. The difference from 100 percent can be taken as a measure of the amount of carboids formed after 80 hours. In no case did the values add up to 100 percent after 80 hours.

It was noted that naphthene aromatics often appeared as two peaks, one major and the other minor. A typical example is given in Graph 3. After aging, the major peak (labeled II)

**Table 6**  
**Iatroscan Analysis of Asphalts After 0-80 hrs. @ 163°C in TGA**

Fraction	Asphalt #	0 hrs.	5 hrs.	20 hrs.	80 hrs.	Asphalt #	0 hrs.	5 hrs.	20 hrs.	80 hrs.
Saturates	1	9.80	8.68	8.38	8.72	11	10.16	10.00	9.26	6.90
Naphthene Aromatics		27.82	15.82	4.68	3.38		21.70	11.91	6.11	1.47
Polar Aromatics		50.80	61.81	52.35	29.98		48.05	54.76	45.82	15.80
Asphaltenes		11.58	13.69	34.59	18.07		20.09	23.33	38.81	1.53
Total		100	100	100	60.15		100	100	100	25.7
Saturates	2	21.39	17.45	14.64	7.19	12	16.06	14.40	12.95	7.42
Naphthene Aromatics		12.46	6.96	3.93	1.19		8.21	6.80	4.59	1.41
Polar Aromatics		35.93	43.68	22.80	18.18		53.47	48.11	28.99	13.69
Asphaltenes		30.22	31.91	18.43	1.65		22.26	30.69	16.46	0.71
Total		100	100	59.80	28.21		100	100	62.99	23.23
Saturates	3	14.22	9.32	9.38	8.84	13	19.87	14.51	12.52	10.09
Naphthene Aromatics		19.48	20.26	20.97	12.32		4.97	3.90	3.06	1.90
Polar Aromatics		50.13	53.89	54.59	30.49		50.63	51.73	39.25	24.16
Asphaltenes		16.17	16.53	15.06	19.65		24.53	29.86	26.64	12.43
Total		100	100	100	71.30		100	100	81.47	48.58
Saturates	4	11.96	10.50	9.63	6.53	14	11.04	10.33	12.53	7.85
Naphthene Aromatics		23.51	18.58	9.09	1.96		13.42	4.04	3.41	1.62
Polar Aromatics		52.20	59.92	55.89	17.74		41.47	42.06	38.72	12.58
Asphaltenes		12.33	11.00	25.49	9.49		34.07	43.57	45.34	1.63
Total		100	100	100	35.72		100	100	100	23.68
Saturates	5	11.93	9.80	9.31	6.24	15	17.35	16.63	13.93	7.46
Naphthene Aromatics		12.00	6.57	4.41	1.51		8.70	5.24	2.90	1.25
Polar Aromatics		59.04	62.41	51.91	18.66		49.47	38.62	21.40	12.71
Asphaltenes		17.03	21.22	34.37	3.00		24.48	39.51	5.86	0.82
Total		100	100	100	29.41		100	100	44.09	22.24
Saturates	6	9.75	6.69	5.72	4.23	16	21.13	16.34	19.46	12.12
Naphthene Aromatics		17.82	7.14	4.15	1.39		12.52	5.45	4.73	2.34
Polar Aromatics		55.58	69.30	55.31	30.96		38.19	43.02	32.40	15.97
Asphaltenes		16.85	16.87	34.82	1.57		28.16	35.19	25.16	1.94
Total		100	100	100	38.15		100	100	81.77	32.37
Saturates	7	9.61	8.96	8.03	6.13	17	16.89	16.52	13.48	12.52
Naphthene Aromatics		16.08	17.62	11.66	2.73		9.73	8.55	4.38	2.32
Polar Aromatics		52.48	46.25	41.78	11.07		44.13	46.72	35.99	18.59
Asphaltenes		21.83	27.17	38.53	5.72		29.25	28.21	46.15	3.54
Total		100	100	100	25.65		100	100	100	36.97
Saturates	8	10.65	9.06	6.90	4.93	18	14.60	13.72	12.43	8.57
Naphthene Aromatics		17.12	11.62	5.37	1.47		11.41	5.26	3.09	1.16
Polar Aromatics		51.10	59.68	43.40	16.92		55.38	51.95	32.30	13.99
Asphaltenes		21.13	19.64	37.28	3.52		18.61	29.07	23.68	2.15
Total		100	100	92.95	26.84		100	100	71.50	25.87
Saturates	9	8.61	9.19	8.27	7.51	19	10.59	10.48	9.85	8.15
Naphthene Aromatics		18.09	12.21	5.15	2.56		16.07	10.97	5.38	2.09
Polar Aromatics		55.98	57.44	42.68	18.56		51.90	53.51	45.83	16.40
Asphaltenes		17.32	21.16	43.90	3.51		21.44	25.04	38.94	2.12
Total		100	100	100	32.14		100	100	100	28.76
Saturates	10	20.73	19.08	16.84	13.57	20	10.33	11.12	11.45	7.29
Naphthene Aromatics		15.72	9.29	5.46	2.07		11.68	10.77	6.84	1.42
Polar Aromatics		43.60	50.76	36.12	17.07		50.37	49.75	42.31	13.97
Asphaltenes		19.95	20.87	41.58	2.44		27.62	28.36	39.40	8.21
Total		100	100	100	35.15		100	100	100	30.89

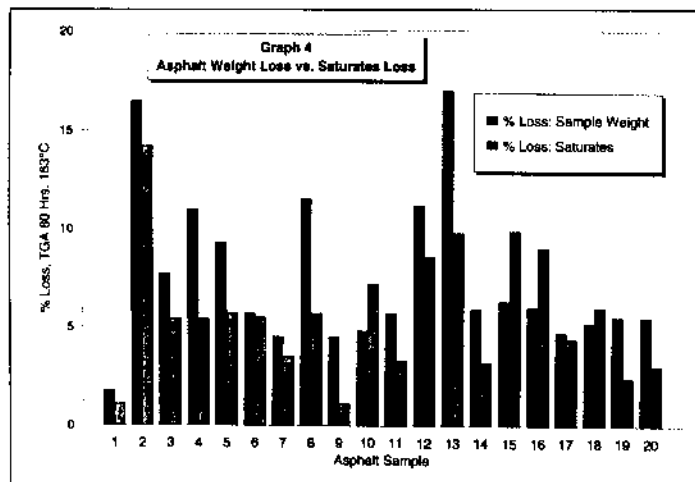
### Scheme 1 Behavior of Asphalt Fractions Toward Oxidation

Saturates → No reaction

Naphthene Aromatics → Polar Aromatics

Polar Aromatics → Asphaltenes

Asphaltenes → "Carboids" ↓

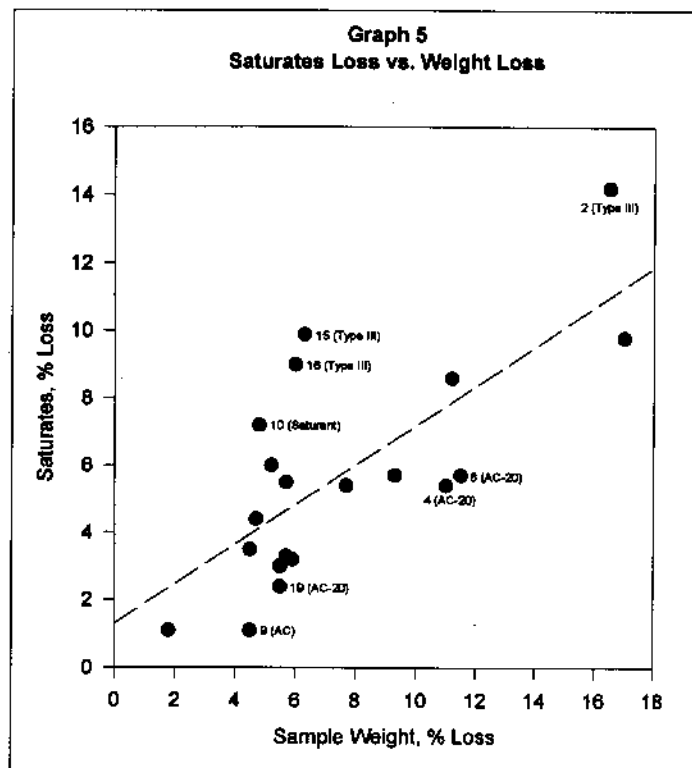


Graph 4.

disappeared more rapidly than the minor peak (labeled I). This suggests that the minor component of the naphthene aromatics is less susceptible to oxidation than the rest of the naphthene aromatics.

The losses in saturates upon heating (Table 6) often bore a relationship to the weight losses observed (Graph 4 and Table 7). In one case, for example, where TGA showed 16.7 percent weight loss in 80 hours, Iatroscan showed a drop of 14.2 percent in saturates content. In another case, where TGA weight loss after 80 hours was only 1.9 percent, the saturates lost 1.1 percent. In a number of cases, the loss in saturates was substantially lower than the total weight loss; it is possible that in such cases a portion of the naphthene aromatics may also be lost through volatilization, but this could not be confirmed by Iatroscan analysis because naphthene aromatics are also known to be converted to polar aromatics under oxidizing conditions (Scheme 1).

Graph 5 provides a plot of percent weight loss in the asphalt sample vs. percent saturates loss. The scatter in this plot suggests that volatilization of saturates does not provide a full explanation for the observed volatilities of asphalts. However, inspection of this plot reveals that the scatter is not randomly distributed. The greatest outliers are labeled in Graph 5. Above the regression line, the greatest outliers are all oxidized asphalts (e.g., Type III), whereas below the regression line, the greatest outliers are paving (AC grade) asphalts. These two types of asphalts differ in their makeup. For example, the paving asphalts contain about 10 to 20 percent asphaltenes, whereas the oxidized asphalts contain about 20 to 30 percent asphaltenes. This difference in com-



Graph 5.

position becomes important in Iatroscan analyses because of a problem of calibration inherent in the flame ionization detector. Combustion of a given weight of saturates will not produce the same number of ions as combustion of the same weight of asphaltenes. This is largely due to the presence of heteroatoms (nitrogen, sulfur, and oxygen) in the asphaltenes that are absent in the saturates. The heteroatoms have a different response factor than carbon in the flame ionization detector. Despite this difference in response factors, the four chromatographic fractions are normalized so that together they add up to 100 percent for each asphalt. It is suggested that the systematic difference in composition between the oxidized and paving asphalts contributes to the scatter in Graph 5. Further work may help to clarify this issue.

## DISCUSSION

The purpose of this work, as noted, is to provide new basic tools to study asphalt volatility and to provide new input that can further elucidate the mechanism of aging on the rooftop. It lies beyond the scope of this work to assess the significance of these data in relation to any particular asphalt roofing product. One inference that may be gained is based upon the thermodynamic rule of thumb that states that reaction rates generally double with a rise in temperature of 10°C (18°F). Diffusion rates are also subject to the same rule. Given the fact that a typical maximum roof temperature is about 83°C (181°F), the TGA temperature of 163°C (325°F) is 80°C (144°F) higher and, therefore, provides eight doublings of the rate, so that an 80-hour test of volatility is thermodynamically equivalent to 2.4 years at a roof temperature of 83°C (181°F). Of course, if the mechanism of volatilization changes at higher temperature, the extrapolation loses validity.

One way in which the reaction mechanism could change is

**Table 7: % Weight Losses (Oven and TGA) and % Saturates Losses (Iatroscan) 80 hrs @ 163°C (325°F)**

Asphalt	% Wt. Loss (Oven)	% Wt. Loss (TGA)	% Saturates Loss (Iatroscan)
1	3.26	1.80	1.08
2	13.63	16.5	14.2
3	11.13	7.70	5.38
4	10.17	11.0	5.43
5	11.94	9.34	5.69
6	5.48	5.70	5.52
7	5.47	4.52	3.48
8	10.18	11.5	5.72
9	5.86	4.55	1.1
10	4.98	4.78	7.16
11	5.49	5.70	3.26
12	11.01	11.21	8.64
13	18.02	17.0	9.78
14	7.94	5.88	3.19
15	5.41	6.26	9.89
16	4.23	6.05	9.01
17	6.09	4.69	4.37
18	3.94	5.21	6.03
19	5.58	5.47	2.44
20	4.86	5.50	3.04

if some molecular cracking reactions take place at 163°C (325°F) but not at 83°C (181°F). Cracking is a thermal process that produces smaller molecules, and this would contribute to volatility. It is likely that some degree of cracking is contributing to the results, particularly in those cases where the weight loss was only partially accounted for by the loss in saturates. However, the overall trends suggest that volatilization of saturates plays a substantial role in weight loss by asphalt.

The wide differences in volatility among the asphalts in this survey, with some losses ranging above 15 percent in 80 hours, should serve to focus interest on the possible role played by volatilization in aging of asphaltic roofing materials. Surface area and layer thickness make a strong contribution to the process, and this suggests that the greatest impact of volatilization will be found in thin products and predominantly at the weathering surface.

## CONCLUSIONS

This paper brings attention to volatility as an element of raw asphalt quality. It is suggested that the role of volatility may have been underestimated in the past because the standard test has been biased by surface effects. In this paper, reexamination of the volatility test procedure has led to the follow-

ing results:

- Volatilities determined by TGA are found to be much greater than those determined by a thick-layer test.
- The TGA results are confirmed by oven agings of thin layer samples.
- Volatility is shown to be a long-term process that does not stop after a few hours.
- Large differences in volatility are seen among various asphalts. Twenty asphalts were surveyed.
- Chromatographic evidence indicates that loss of saturates is a major contributing factor to volatilization.

In the roofing industry, substantial efforts have been devoted over many years to address the mechanisms of deterioration, including cracking, embrittlement, thermal expansion and contraction stresses, and the like. The present results suggest that embrittlement and cracking might also be induced by yet another mechanism, namely volatilization, that until now has received little attention. Losses of only a few percent could evoke volume changes that might cause significant cracking. Certain types of roofing products, such as those that do not contain polymers to help accommodate stresses induced by shrinkage, are more likely to be susceptible to the effects of volatilization. If these effects are important, the present results suggest that years of weathering might be modeled in laboratory experiments that can be completed in a few days. The choice of asphalt in a roofing product could be significant; this work has demonstrated large differences in behavior among various asphalts. If one asphalt loses 17 percent of its weight and another loses only 1 percent over its lifetime, further investigation may be warranted. The roofing industry in the 21st century may benefit from further study of the role of volatilization in the aging of roofing products. Modern analytical tools, such as thermogravimetric analysis and Iatroscan chromatography, will facilitate that effort.

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