

# Inverse GLC—An Extension of the Technique to The Study of Oxidation of Asphalts

T. C. DAVIS and J. C. PETERSEN

Respectively, Research Chemist, and Project Leader, Laramie Petroleum Research Center, Bureau of Mines, Laramie, Wyoming

An extension of the inverse GLC technique to the study of the oxidation of asphalts is reported. In the new approach, an asphalt, serving as the liquid substrate in a gas liquid chromatographic column, is oxidized directly within the chromatograph. The retention behavior of a group of selected test compounds possessing different functional groups is determined before and after oxidation. Because the retention behavior is dependent on interactions between the functional groups of the test compound and chemical functionalities in the asphalt, the changes occurring in the asphalt on oxidation are reflected as changes in retention behavior. Inverse GLC was found sensitive in detecting changes that take place on oxidation, and holds promise as a method of predicting asphalt durability.

•THE USE of inverse gas liquid chromatography (GLC) as a technique for studying petroleum asphalts has been previously outlined by Davis, Petersen, and Haines (1). The present paper presents an extension of this technique by which the oxidation of asphalts can be studied.

In the application, the retention behavior of carefully selected volatile test compounds of known chemical composition is determined on an asphalt stationary phase. The asphalt column is then oxidized in place within the GLC instrument, and the retention behavior of the test compounds is again determined. Retention behavior of the test compounds is largely determined by interactions between the test compounds and the chemical functionality of the asphalt; thus, changes in the behavior of the test compounds upon oxidation reflect changes in the chemical composition of the asphalt.

This report covers preliminary oxidation studies using the six asphalts from the original work by Davis et al. (1), plus six roofing asphalts previously characterized by Greenfeld and Wright (2). The latter group of asphalts forms the basis for correlations between changes in test compound retention behavior on asphalt oxidation and durability.

## EXPERIMENTAL

### Apparatus

GLC data were obtained on a Beckman GC-2\* gas chromatograph that was modified to allow diverting the carrier gas and substituting compressed air during oxidation. The instrument was also modified to allow bypassing the column detector during the oxidation step.

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\*References to specific commercial materials or models of equipment in this report are made to facilitate understanding, and do not imply endorsement by the Bureau of Mines.

## Procedure

A  $\frac{1}{4}$ -in. by 13-ft GLC column was packed with one part of asphalt on 10 parts by weight of Fluoropak 80 and conditioned for a minimum of 6 hr under normal operating conditions using a helium inlet gage pressure of 15 psi and an instrument operating temperature of 130 C. Following conditioning, the test compounds were introduced as previously described (1). The asphalt was then oxidized within the column by replacing the helium carrier gas with filtered air at an inlet gage pressure of 15 psi (flow rate approximately 30 ml/min). The column temperature was maintained at 130 C for an oxidation period of 24 hr. (Other oxidation conditions were investigated and are discussed later.) Following oxidation, normal operating conditions were reestablished and the column conditioned for a minimum of 2 hr. Test compound retention data were then obtained on the oxidized column.

To quantify the test compound retention data, and thus provide for data comparison, the data were calculated as interaction coefficients (1). (The interaction coefficient,  $I_p$ , is 100 times the logarithm of the corrected retention volume of the test compound, minus 100 times the logarithm of the corrected retention volume of a hypothetical n-paraffin of equivalent molecular weight, both values determined on the asphalt.) The oxidation data are reported as the change on oxidation, or  $\Delta I_p$ , which is equal to the  $I_p$  obtained on the oxidized asphalt minus the  $I_p$  obtained prior to oxidation.

## DISCUSSION OF EXPERIMENTAL TECHNIQUES

Oxidation of asphalts in the GLC offers a technique for the examination of small samples, gives easy control over temperature and air flow rate, and eliminates the additional handling required for separately oxidized samples. In addition, oxidation of asphalt in a GLC column provides a method of exposing large surface areas.

During the oxidation of the asphalt, the concentration of the oxygen in the air may vary along the column length due to both its reaction with the asphalt and the normal pressure drop through the column. In order to minimize the change in concentration resulting from reaction of oxygen with the asphalt, it is necessary that the exit gas contain nearly the same concentration of oxygen as the inlet gas. Three different oxidation conditions were evaluated as shown in Figure 1, in which the percent of unreacted oxygen in the column exit stream is plotted as a function of time. These data were obtained by GLC analyses of the exit gases on a molecular sieve column. Of the oxidation conditions shown, only at 130 C and 30 ml/min air flow rate (corresponding to 15-psi inlet gage pressure) does the amount of unreacted oxygen in the column exit stream approach that in the air entering the column. At 200 C, a high percentage of the oxygen in the air passing through the column was consumed by the asphalt, thus contributing significantly to a nonuniform oxidation. This nonuniform oxidation was also evidenced by a darkening of the asphalt packing at the front end of the column, and by differences in benzene solubility along the column length. The actual pressure drop through the column at the 30 ml/min air-flow rate was measured to determine its effect in producing an oxygen concentration differential along the column. Although the absolute gas-inlet pressure of the instrument was 26.2 psia (15 psi instrument gage reading at Laramie, Wyoming, where atmospheric pressure averages 11.2 psia), the actual inlet and outlet pressures of the column averaged 17.5 psia and 13.5 psia, respectively. The additional pressure drops between the 26.2-psia inlet pressure and 11.2-psia atmospheric pressure are accounted for primarily by capillary restrictions inherent within the GLC instrument. The measured 4.0-psi pressure drop through the column thus produces a drop in oxygen concentration of 23 percent. The total combined drop in oxygen concentration along the column length due to both chemical reaction and pressure drop for a typical asphalt was thus estimated at 25-30 percent, when operating at 130 C and 30 ml/min air-flow rate.

Test compounds were run on asphalt columns (both unoxidized and oxidized) before and after 48-hr thermal treatments to determine the possibility of significant mechanical or chemical changes occurring in the columns at test temperatures due to heat alone. Results of these tests indicated 130 C to be a safe operating temperature to avoid significant thermal changes.

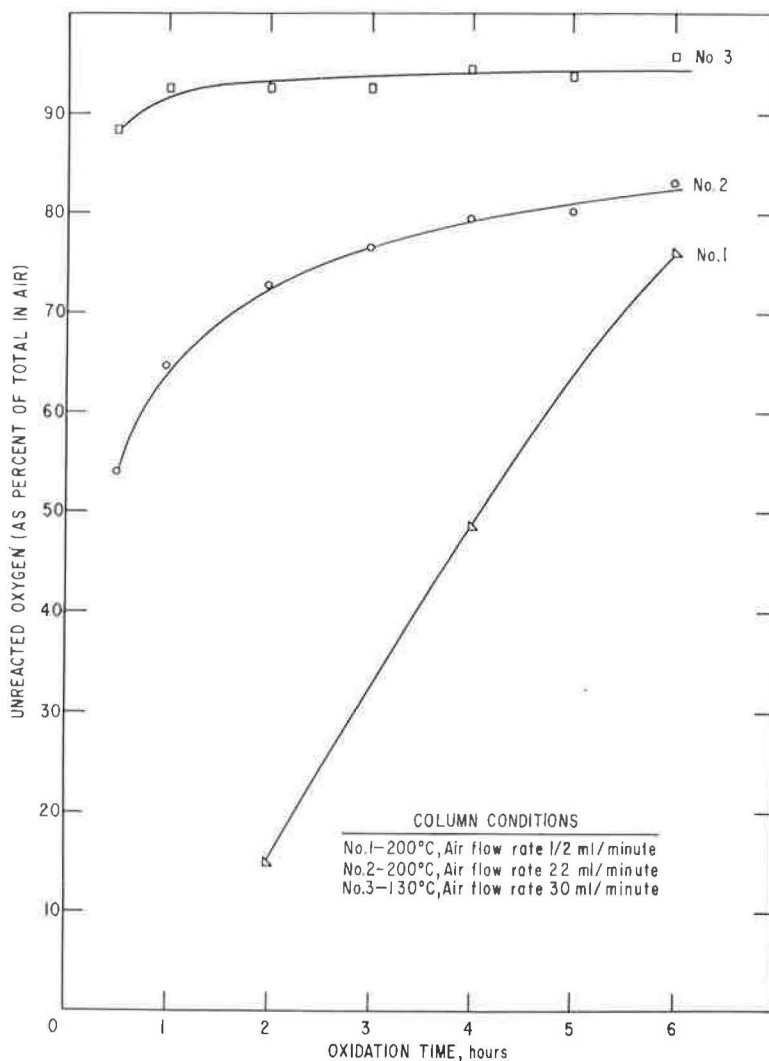


Figure 1. Oxygen in column exit gas during air oxidation.

To determine if test compounds reacted with the asphalts and thus altered the course of subsequent oxidation, asphalts were oxidized both before and after exposure to test compounds. Test compound retention data showed no significant differences.

## RESULTS AND DISCUSSION

### Types of Forces in Inverse GLC

In inverse GLC, the test compound retention behavior is governed to a large degree by intermolecular forces between the test compound and the asphalt. The forces to be considered in gas liquid chromatography can be grouped into four types (3).

1. London, or dispersion, forces. These are intermolecular forces between two nonpolar substances, and arise from synchronized variations in the instantaneous dipoles of the two interacting substances. They are present in all cases, and are the only attraction forces between two nonpolar substances.

2. Debye, or induced dipole forces. These forces result from the interactions of a permanent dipole with an induced dipole in a neighboring molecule. The size of such forces is usually small.

3. Keesom, or orientation, forces. These are orientation forces which arise from the interaction of two permanent dipoles. Among these is the "hydrogen bond."

4. Chemical bonding forces arising from the formation of loose chemical adducts.

An understanding of the interactions of the test compound with the asphalt in terms of the forces involved would be most useful in providing information about the chemical composition of asphalt and the products formed on oxidation.

In the method used for calculating inverse GLC data (1), test compound retention behavior is referenced to the behavior of normal paraffins on asphalt. Normal paraffins generally exhibit only London, or dispersion forces; therefore, these forces are not significantly reflected in the interaction coefficients reported. As a result, the interaction coefficients, and the changes in  $I_p$  on oxidation, are essentially a measure of the stronger forces resulting from induced and permanent dipoles and chemical bonding forces. Inverse GLC, therefore, is particularly adaptable to the study of functional groups (which are often strongly polar) initially present or produced in the asphalt on oxidation. The freedom to choose from a variety of test compounds adds versatility to the method and makes possible the collection of many bits of information about the composition of the asphalt without prior fractionation.

#### Changes in Asphalt on Oxidation as Indicated by Inverse GLC

Interaction coefficient data for 24-hr, 130 C oxidation studies are shown in Table 1 for the six asphalt samples used in the original work (1). The individual test compound data obtained on the unoxidized asphalts ( $I_p$ ) and the change on oxidation ( $\Delta I_p$ ) are shown. The test compounds in Table 1 have been arranged in the order of increasing  $\Delta I_p$  on asphalt No. 1. Examination of the data indicates that the relatively nonpolar and non-polarizable compounds near the top of the table are nearly insensitive to oxidation changes in asphalt. Those compounds that would be expected to interact with oxygen containing groups produced in asphalt on oxidation show large changes in interaction coefficients. For example, butanol, propionic acid, and phenol have both oxygen and hydrogen which can share in hydrogen bonds with groups formed in the asphalt. These

TABLE 1  
EFFECTS OF ASPHALT OXIDATION ON TEST COMPOUND RETENTION BEHAVIOR

Test Compound	Interaction Coefficient ( $I_p$ ) <sup>a</sup>						Change on Oxidation ( $\Delta I_p$ ) <sup>b</sup>					
	Asphalt No.						Asphalt No.					
	1	2	3	4	5	6	1	2	3	4	5	6
Methylcyclohexane	24	23	24	24	23	29	-1	3	-1	-2	1	3
Toluene	47	47	51	48	43	69	0	5	0	2	5	9
2-Methyl-2-pentanethiol	4	2	6	3	1	22	0	3	0	2	4	6
2-Thiahexane	40	42	45	43	38	58	1	0	0	0	2	5
Allyl ether	5	3	8	7	2	30	1	4	3	0	3	3
1-Decane	4	2	3	2	2	8	2	-1	2	1	0	-1
Heptaldehyde	34	33	42	37	25	68	2	3	-1	0	4	2
Butyl acetate	-2	-3	5	0	-5	25	2	1	0	2	2	10
2-Methylpyridine	61	62	71	69	56	98	2	10	-1	0	0	2
Butanol	44	45	60	51	41	71	5	17	3	7	3	11
Propionic acid	73	83	128	99	63	75	9	19	10	3	12	25
Pyrrole	86	89	108	94	80	124	12	20	9	11	13	26
Formamide	127	132	164	149	118	179	14	34	17	15	22	50
Phenol	118	120	147	125	106	138	30	50	15	27	15	40
1-Methylpyrrolidine	36	37	42	50	36	61	113	167	79	143	88	27

<sup>a</sup>Before oxidation.

<sup>b</sup>Asphalt oxidized 24 hr, 130 C, 15 psi air inlet pressure.

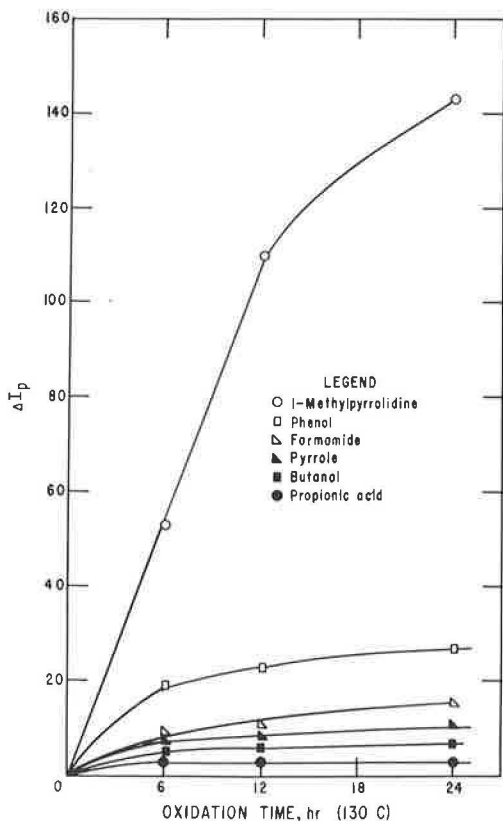


Figure 2. Changes in interaction coefficient ( $\Delta I_p$ ) on oxidation (asphalt No. 4).

compounds also show significant  $\Delta I_p$ 's. In addition, the strongly basic amines would be expected to interact with acid groups produced on oxidation, and the data do show 1-methylpyrrolidine to be held more tightly (higher  $\Delta I_p$ 's) than the acidic test compounds. Although not shown in Table 1, the additional strong bases, triethylamine, piperidine, and cyclohexylamine, were usually held so tightly by the oxidized columns that  $\Delta I_p$ 's were not obtained. In contrast, the weaker base 2-methylpyridine showed relatively small  $\Delta I_p$ 's. These differences in behavior of the organic bases may be indicative of the acid strength of the oxidation products.

The changes in the interaction coefficients resulting from the oxidation of asphalt No. 4, as a function of oxidation time, are shown in Figure 2. The change in the interaction coefficient of the basic 1-methylpyrrolidine is in sharp contrast to the changes produced with the remainder of the test compounds shown. 1-Methylpyrrolidine has a high rate of increase in  $\Delta I_p$  and does not begin to show a significant change in the rate of increase until after 12-hr oxidation. The other test compounds which contain more acidic groups show maximum change in  $\Delta I_p$  during the first 6 hr of oxidation and then level off. These data suggest that different oxidation products are detected by the basic and acidic test compounds, and that the concentra-

tions of these products vary with the level of oxidation.

The oxidation-inverse GLC technique was able to show differences in the chemical characteristics of asphalts that were not observable by most common characterization tests. Asphalts Nos. 1 and 2 in Table 1 showed similar softening points, penetrations, carbon residues, elemental analyses, and oil, resin, and asphaltene contents (1). Their interaction coefficients prior to oxidation were also similar. However, their oxidation characteristics were not the same, as shown by the differences in the  $\Delta I_p$  values. Asphalt No. 2 is apparently much more susceptible to oxidation, and may have significantly different weathering properties.

A well-known path in the oxidation of hydrocarbons involves the removal of a hydrogen atom from a carbon atom, followed by the uptake of oxygen by the hydrocarbon radical formed, ultimately leading to polar, oxygen-containing functional groups. The presence of reactive hydrogen labile toward this reaction would probably not be detected by inverse GLC prior to oxidation, because of the weak interaction forces of the hydrocarbon fragment. It is not surprising, therefore, that two asphalts may have similar interaction coefficients prior to oxidation, and different interaction coefficients following oxidation. Inverse GLC should be useful in detecting this type of reactivity; however, the changes in  $I_p$  observed on oxidation are by no means restricted to interactions with the products of hydrocarbon oxidation as in the example cited.

#### Correlation with Durability

Greenfield and Wright (2) showed correlative trends between asphalt durability (as measured by the carbon-arc accelerated-weathering machine) and asphaltene content,

TABLE 2  
PROPERTIES OF GREENFELD AND WRIGHT ASPHALTS<sup>a</sup>

Asphalt No. b	Softening Point, F	Penetration, 0.1 mm, 75 F	Specific Gravity at 77 F	Durability, Days <sup>c</sup>
GW-2, Tia Juana-Lago Colon	220	17	1.017	69
GW-3, California Coastal (catalyzed)	221	18	1.032	53
GW-5, Kansas-Indiana	212	21	1.010	95
GW-9, California Coastal (fluxed)	230	20	1.026	32
GW-19, Kansas	223	16	1.005	95
GW-22, Lagunillas	224	14	1.030	60

<sup>a</sup>Data from Greenfeld and Wright (2).

<sup>b</sup>Sample designations are Greenfeld and Wright numbers prefixed with GW.

<sup>c</sup>Using carbon-arc accelerated weathering machine in accordance with daily cycle A in Recommended Practice for Accelerated-Weathering Test of Bituminous Materials (D529-59T), 1961 Book of ASTM Standards, Part 4, p. 1233.

TABLE 3  
INVERSE GLC RESULTS ON GREENFELD AND WRIGHT ASPHALTS

Test Compound	Interaction Coefficient ( $I_p$ ) <sup>a</sup>						Change on Oxidation ( $\Delta I_p$ )					
	Asphalt No.						Asphalt No.					
	GW-9	GW-3	GW-22	GW-2	GW-5	GW-19	GW-9	GW-3	GW-22	GW-2	GW-5	GW-19
Triethylamine	2	28	-3	-4	1	-1	>150	107	111	104	42	39
1-Decane	3	2	2	2	2	2	-1	1	1	0	0	1
Methylcyclohexane	21	21	20	20	20	19	0	1	1	0	1	1
Butanol	51	51	48	40	44	43	7	4	6	10	3	4
Pyrrole	94	94	91	82	86	82	16	11	11	15	6	7
Propionic acid	96	87	81	65	71	66	17	18	10	16	2	5
Phenol	137	126	129	108	117	110	31	27	22	33	9	12
Formamide	149	150	141	123	136	131	28	12	16	23	15	10

<sup>a</sup>Before oxidation.

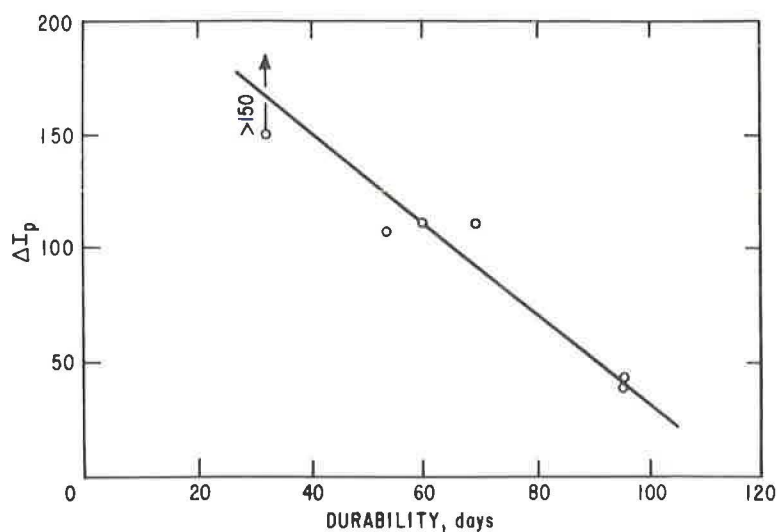


Figure 3. Relationship between accelerated weathering durability and change in interaction coefficient ( $\Delta I_p$ ) for triethylamine on 130°C air oxidation (durability data obtained by Greenfeld and Wright).

rate of filtration, solubility parameter, and carbonyl index. These investigators studied air-blown roofing asphalts.

To determine if inverse GLC retention data correlated with asphalt durability, a survey was conducted on six of the asphalts investigated by Greenfeld and Wright. These asphalts were chosen to cover a wide range of durabilities. Selected properties are shown in Table 2. Interaction coefficients for the six asphalts and the change in these coefficients on oxidation, using test compounds representing a wide range of activity, are shown in Table 3. Asphalts are arranged from left to right in order of increasing durability. Test compounds are arranged according to increasing  $I_p$  on asphalt GW-9.

Correlative trends were found between durability and the change in interaction coefficients on oxidation ( $\Delta I_p$ ) with several of the test compounds. For example, results obtained with triethylamine, plotted in Figure 3, show an inverse relationship between the variables. While the primary purpose of this paper is to report the inverse GLC oxidation technique and to suggest its usefulness in studying chemical changes occurring in asphalt on oxidation, the correlation with durability indicates its usefulness in establishing empirical relationships.

### SUMMARY AND CONCLUSIONS

Inverse GLC offers a new technique for the study of the oxidation of asphalts. Differences among asphalts, and differences in their behavior on oxidation, are readily detectable. By following the changes in interaction coefficients, changes in asphalt chemical functionality on oxidation (and thus differences in the oxidation characteristics of asphalts) may be detected. An understanding of these changes should be useful in studying the initial chemical composition of the asphalt. Results of accelerated weathering of asphalts indicate inverse GLC to be useful in predicting asphalt durability.

### REFERENCES

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