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EFFECT OF ATMOSPHERIC PRESSURE ON OZONE CRACKING OF RUBBER

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SUMMARY

Ozone chamber testing of rubbers occupies a prominent place in the field of polymeric degradation testing. In such testing the rate of ozone cracking of rubber vulcanizates is a function of the rate of collision of ozone molecules with the rubber surface, all other factors constant. However, the conventional mode of expression of the ozone concentration in chamber testing is on a volume O_3 *per volume air basis, i.e. parts* O_3 *per hundred million* (10^8) *air by volume, abbreviated by pphm.*

In this paper we show that at equal ozone concentrations expressed as pphm, cracking rate is a function of the ambient atmospheric pressure (in the chamber). Thus variations in ozone test results may occur in intra- or inter-laboratory testing if ambient atmospheric pressure at the time or place of test is sufficiently different. A mode of expression that avoids this is recommended, i.e. the partial pressure of O_3 *in mPa.*

INTRODUCTION

The testing of compounded, cured rubbers for ozone cracking resistance occupies a prominent place in the general scheme of polymeric degradation testing. The failure of rubber products in service is often the direct result of the ozone induced surface cracking or alternatively fatigue or mechanical failure is initiated by the surface cracks produced by ozone attack.

Rubbers are most frequently evaluated for their ozone crack resistance by exposure to ozonated air in laboratory testing chambers. Such chambers

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nominally consist of

1. a thermostat and heater system to control testing temperature;
2. a chamber air circulation system in equilibrium with atmospheric pressure (internal fan or other device);
3. an ozone generator, most frequently a mercury vapor UV light source which generates ozone as an air stream is passed through it.

Analysis of the ozone content in the chamber air is conducted by a variety of techniques; electrochemical,[1] UV light absorption,[2] chemiluminesence[3,4] and absorption of the ozone by reaction with iodide ion in a neutral buffered aqueous solution.[5,6] The iodide ion is oxidized to free iodine by the ozone and the iodine is titrated with standardized sodium thiosulfate solution.

National standard test methods for ozone testing such as ASTM D-1149-77T and BS 903 as well as the international standard ISO 1431 express ozone concentration in the air of the chamber on a volume per volume basis. Nominally the ozone concentration is expressed in parts of ozone per 100 million (10^8) parts of air (by volume). This is abbreviated by the term pphm, parts per hundred million.

This paper illustrates a testing error that can occur when the pphm (volume) basis of ozone concentration is used. In intra-laboratory testing (at different times), one source of variation in test results is the fluctuation of atmospheric pressure. In inter-laboratory testing, similar test variations can be attributed to atmospheric pressure differences due to geographical location, i.e. elevation above sea level. The latter effect is especially important in producer v. industrial consumer ozone testing for quality control and specification purposes.

BACKGROUND ON THE PROBLEM

The rate of ozone reaction with rubber (or the cracking rate of rubber) is a function of the collision rate of ozone molecules with the rubber surface, all other factors constant. A change in barometric pressure, at constant temperature, will alter this collision rate even if the ozone content in the chamber is maintained constant on a volume (ozone) per unit volume (air) basis. Therefore, ozone content or concentration cannot be unambiguously expressed on a volume per volume basis in situations where differences in atmospheric pressure are likely. A method of expressing ozone content that is free of this limitation must be used. This atmospheric pressure effect was discovered by one of us (RLE) as part of a continuing inter-laboratory testing program of the Gates Rubber Co.

The testing as outlined here was conducted as part of an ASTM sponsored program to modify the ASTM D-1149 Standard. Two laboratories were selected to participate; BF Goodrich R & D Center, designated Lab-1, and Gates Rubber Co., designated as Lab-2 in some of the tables and figures that follow. The nominal pressure differential between these two locations is 13·3 kPa (100 torr).

It was realized that there would be two requirements for the successful execution of this inter-laboratory testing program.

1. A quantitative method for measuring the degree of ozone cracking.
2. Accurate measurement of O_3 concentration in both laboratories.

To meet both of these requirements, actions were taken as outlined in the Inter-laboratory Test Procedure section listed in the appendix. Briefly stated, the degree of ozone cracking was assessed by the SOC technique[7] and tests were conducted at three target ozone concentrations in the range 30–70 pphm and then comparisons made at exact concentrations of 30, 50 and 70 ± 1 pphm. This avoids the tedious task of requiring each laboratory to obtain exact ozone concentrations by numerous adjustments. It is suggested that the Inter-laboratory Test Procedure be consulted prior to the next section of test results. The SOC value is a numerical expression of the size of ozone cracks and is measured by a microscopic technique. It is the product of the average length and width of a selected representative sample of the surface ozone cracks.

TEST RESULTS

Four compounds were prepared that provided for moderate degrees of ozone cracking in test chamber exposure periods of 2 and 4 h at the selected ozone levels. The formulations are listed in Table 1. The measured SOC values at 2 and 4 h of ozone chamber exposure were used to prepare plots of SOC v. ozone concentration.

Table 2 lists SOC values at exact ozone concentrations of 30, 50 and 70 pphm as interpolated from plots of log (SOC) v. O_3 as shown in Figs. 1 to 4. The log (SOC) transformation gives, in most cases, an essentially linear plot. This quasi-linear behavior assists in interpolation. The log (SOC) parameter expresses the degree of ozone cracking damage due to variations in ozone partial pressure at the two test laboratories that most nearly is a linear function of ozone concentration. The log transformation is intended to apply over the range of 30–70 pphm only and no fundamental implication is intended in this particular dependency. An obvious problem is the non-zero SOC value at zero ozone concentration implied by the observed logarithmic dependence.

TABLE 1
TEST FORMULATIONS

	A	B	C	D
SBR-1502	100·0	100·0	—	—
SBR-1708	—	—	137·5	137·5
N285 carbon black	50·0	50·0	75·0	75·0
Zinc oxide	5·0	5·0	5·0	5·0
Stearic acid	1·0	1·0	1·0	1·0
Sulfur	2·0	2·0	2·0	2·0
TBBS[a]	1·0	1·0	1·25	1·25
Santoflex AW[b]	1·0	2·0	—	2·0
UOP-288[c]	—	—	1·0	—

[a] *n*-*t*-Butyl-2-benzothiazole.
[b] Ethoxy dihydrotrimethyl quinoline.
[c] Dimethyl heptyl p-phenylenediamine.
Note: Test specimens were cured 45 min at 150 °C.

TABLE 2
SOC VALUES AT INDICATED CONDITIONS[a]

Compound	*Hours exposed*	30 *pphm* *Lab*-1	30 *pphm* *Lab*-2	50 *pphm* *Lab*-1	50 *pphm* *Lab*-2	70 *pphm* *Lab*-1	70 *pphm* *Lab*-2
A	2	4·4	1·7	6·2	6·2	12·0	14·5
	4	14·5	10·5	29·0	21·0	75·0	42·0
B	2	2·9	1·5	6·1	3·1	14·5	7·1
	4	16·0	8·8	25·0	16·0	44·0	27·0
C	2	3·3	2·1	6·3	4·2	13·0	9·0
	4	11·2	8·8	18·5	13·0	32·0	21·0
D	2	3·3	2·1	6·9	4·7	15·0	11·0
	4	11·2	7·0	19·0	12·5	33·0	23·0

Average atmospheric pressure: Lab-2, 636 torr (84·7 kPa); Lab-1, 736 torr (98·1 kPa).
[a] Values interpolated from plots of measured SOC v. O_3 concentration.

On this basis the log (SOC) values were obtained (see Table 3), and from these data, ratios were obtained and used to prepare Table 4. The ratios represent the difference in degree of ozone damage in the two laboratories or at the two atmospheric pressures; 736 torr (98·1 kPa) at Lab-1 and 636 torr (84·7 kPa) at Lab-2.

The expected effect of a reduction in pressure when the ozone concentration is maintained constant, pphm by volume, is a reduction in the collision rate (or partial pressure) of ozone molecules with the rubber surface. The ratio of air or total pressures will also be the same ratio as the O_3 partial pressures, therefore:

$$\text{Expected Effect Ratio} = \frac{P_2}{P_1} \tag{1}$$

where P_1 = lower pressure and P_2 = higher pressure. In this situation the

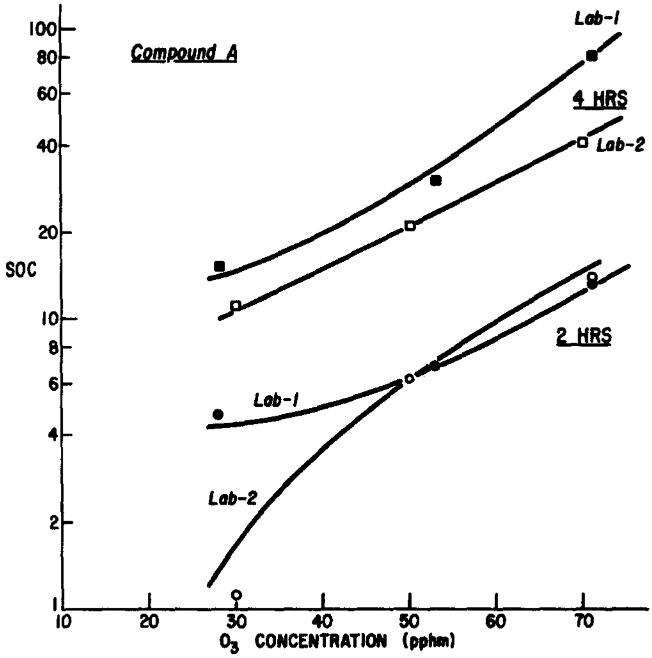

Fig. 1. Log (SOC) v. ozone concentration for Compound A.

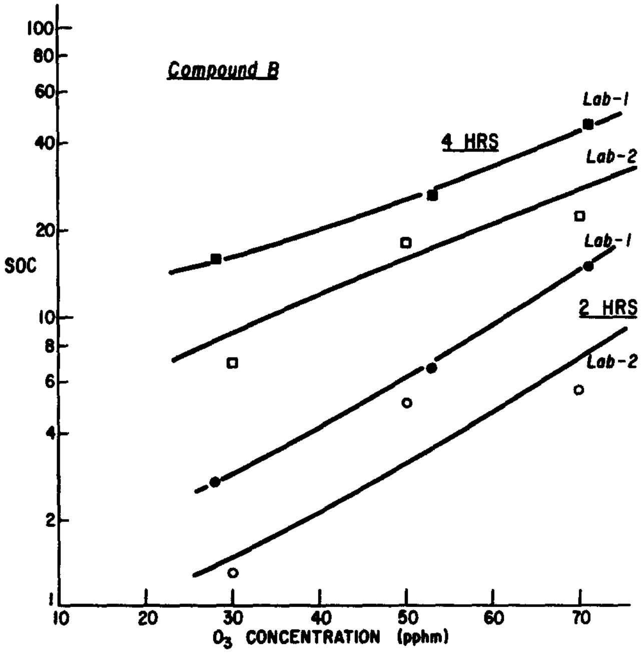

Fig. 2. Log (SOC) v. ozone concentration for Compound B.

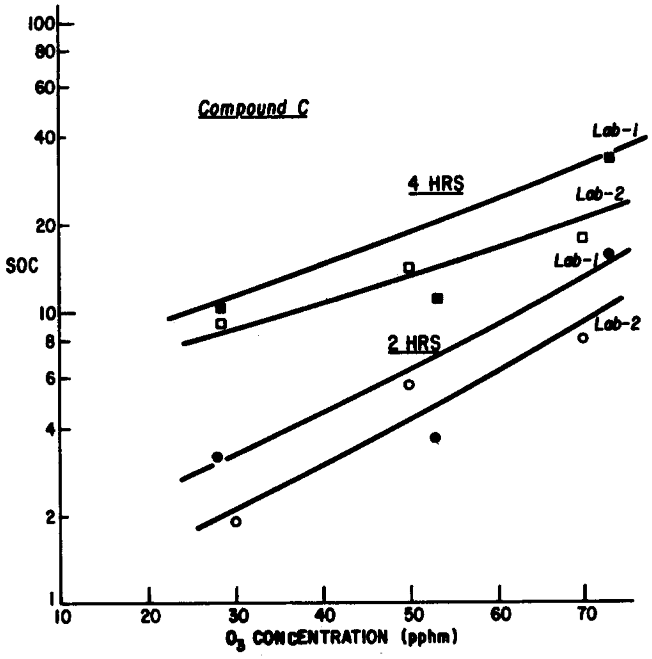

Fig. 3. Log (SOC) v. ozone concentration for Compound C.

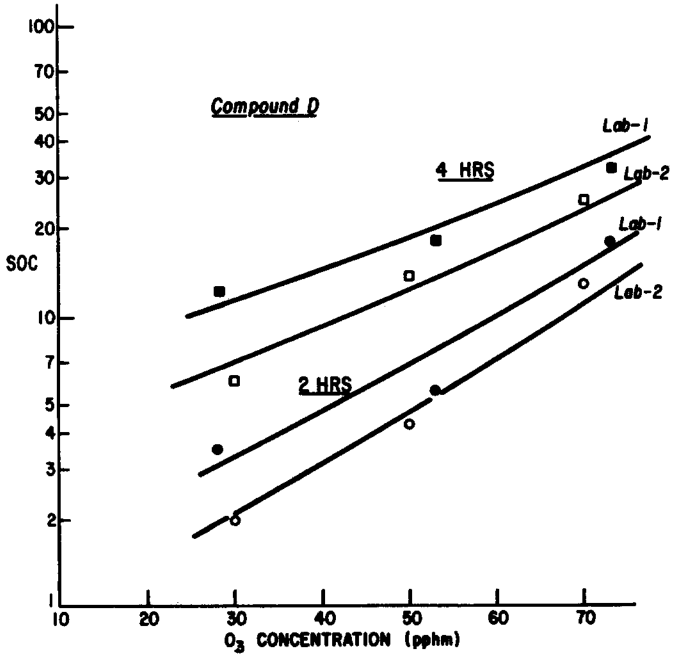

Fig. 4. Log (SOC) v. ozone concentration for Compound D.

TABLE 3
LOG (SOC) VALUES AT INDICATED CONDITIONS[a]

Compound	*Hours exposed*	*30 pphm* *Lab*-1	*30 pphm* *Lab*-2	*50 pphm* *Lab*-1	*50 pphm* *Lab*-2	*70 pphm* *Lab*-1	*70 pphm* *Lab*-2
A	2	0·643	0·230	0·792	0·792	1·079	1·161
	4	1·161	1·021	1·462	1.322	1.875	1·623
B	2	0·462	0·176	0·785	0·491	1·161	0·851
	4	1·204	0·944	1·398	1·204	1·643	1·431
C	2	0·519	0·322	0·799	0·623	1·114	0·954
	4	1·049	0·944	1·267	1·114	1·505	1·322
D	2	0·519	0·322	0·839	0·672	1·176	1·040
	4	1·049	0.845	1.279	1.097	1·519	1·362

[a] Interpolated (scaled) values from plots of measured SOC v. O_3 concentration. Common or base 10 logarithms used.

TABLE 4
(LAB-1/LAB-2) LOG SOC

Compound	*Hours*	*30 pphm*	*50 pphm*	*70 pphm*
A	2	2·79	1·00	0·93
	4	1·14	1·11	1·16
B	2	2·62	1·60	1·36
	4	1·28	1·16	1·15
C	2	1·61	1·28	1·17
	4	1·11	1·14	1·14
D	2	1·61	1·25	1·13
	4	1·24	1·17	1·12
Average 2 h		2·16	1·28	1·15
Average 4 h		1·19	1·15	1·14

atmospheric pressures are $P_1 = 636\ \text{torr} = 84{\cdot}7\ \text{kPa}$ and $P_2 = 736\ \text{torr} = 98{\cdot}1\ \text{kPa}$.

$$\text{Expected Effect Ratio} = \frac{736}{636} = 1{\cdot}16 \qquad (2)$$

Thus a 16% increase in cracking rate or in extent of cracking at a fixed ozone chamber exposure time is to be expected at the higher atmospheric pressure test site. Table 4 lists the ratios of log (SOC) Lab-1 v. Lab-2 or at pressures of 736/636 for all three nominal ozone levels.

The ratios vary from a maximum of 2·79 to a minimum of 0·93. The values for Compound A at 2 h appear to be slightly in error. However, taking all values and forming averages for the 2 and 4 h periods for all four compounds, the entries at the bottom of the table are obtained for each target ozone level. The values for 2 h at 30 and 50 pphm target levels are somewhat higher than the expected ratio of 1·16, but the 70 pphm 2 h value and all 4 h values are in good agreement.

The reason for the high values can be explained if it is realized that an induction period precedes the actual appearance of ozone cracks and their subsequent growth with continued exposure. Figure 5 explains this. If tests are carried out at two atmospheric pressures P_1 and P_2 with $P_2 > P_1$, then since the collision rate will be greater at P_2, its induction period will be shorter, shown by t_2 in Fig. 5. The cracks will grow as indicated by the P_2 curve; at some later time the specimen at P_1 will begin to crack (longer induction period) and grow at a slightly lower rate.

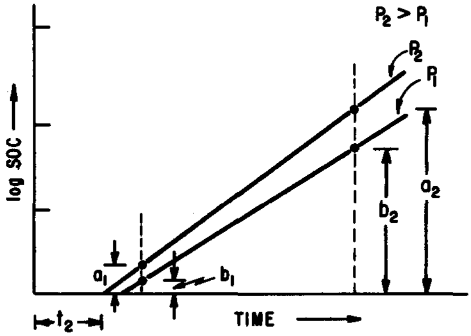

Fig. 5. Schematic representation of cracking rate curves at two laboratory atmospheric pressures.

If the extent of cracking ratio, P_2 v. P_1, is formed at a point in time near the induction periods with the values a_1/b_1 as indicated, it is readily apparent that this ratio will be larger than the ratio a_2/b_2, formed at some point in time well removed from the induction period. The point defined by a_2 and b_2 is in the region of constant proportional difference or ratio. Thus the reason for the large experimental average ratios in Table 4 is clear. They are obtained near the induction times. The lower the nominal O_3 level and the shorter the chamber exposure time the closer is any point in question to the induction period.

If we may roughly equate chamber exposure time and nominal O_3 concentration, we can form their product as a measure of the 'severity' of ozone exposure. In taking products of nominal O_3 concentration and time, the values shown in Table 4 were used.

If the ratio of log (SOC) at the two pressures is plotted v. the concentration × time product, the curve of Fig. 6 is obtained. This shows that beyond a product value of 140 the theoretical or expected ratio of 1·16 (shown by arrow) is closely approximated by the experimental ratios.

Thus the data strongly substantiate the simple theoretical analysis on collision rates and show that although nominal ozone concentrations (pphm by volume) as measured by the current ozone analysis technique are equal, ozone attack or cracking will not be equivalent if atmospheric pressures and consequent O_3 partial pressures are not equal.

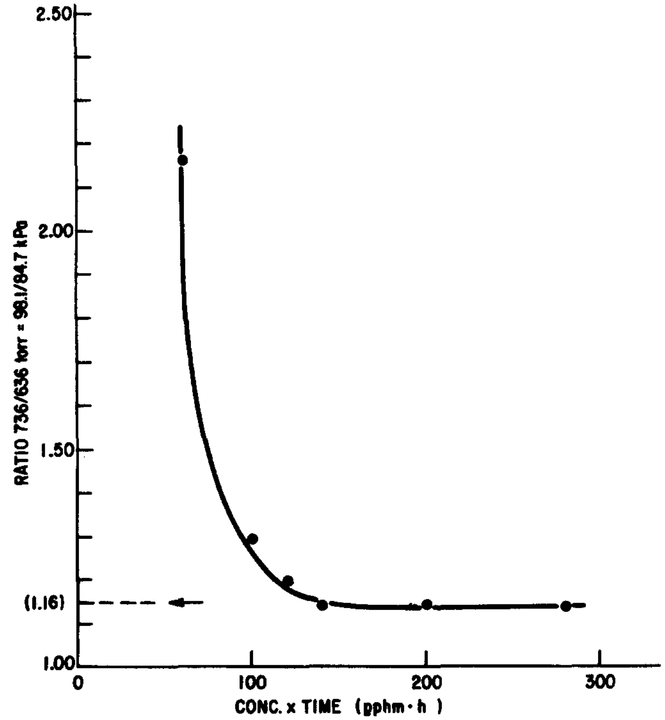

Fig. 6. Log (SOC) ratio at 736 torr (98·1 kPa)/636 torr (84·7 kPa) v. the severity of ozone exposure, i.e. O_3 concentration × time.

A PROPOSAL TO CORRECT THE PROBLEM

A resolution to the volume/volume expression of ozone content can be accomplished by the application of Dalton's law and the gas equation. The ozone partial pressure is used to express ozone content or activity. The partial pressure of ozone in the mixture with air is given in mPa, by

$$P(O_3) = n(O_3)\frac{RT}{V} \tag{3}$$

where $n(O_3)$ = number of moles of O_3 (in volume V), R = gas constant (8·312 mPa m^3/K), T = temperature (K), V = volume of air–ozone mixture sampled (m^3).

The evaluation of $n(O_3)$ is made on the basis of any of the analytical methods[1–6] cited earlier. Temperature T is directly measured and the volume sampled, V, is evaluated from flowmeter × time data suitably corrected for ambient atmospheric pressure conditions.

This particular mode of expressing ozone content, which is responsive to variations in atmospheric pressure, yields a good correspondence to nominal pphm values under standard conditions of temperature and pressure. Thus at 760 torr (1 atm.) or 101 kPa and at 273 K

$$1\ \text{pphm} = 1{\cdot}01\ \text{mPa} \tag{4}$$

At 25 °C (nominal room temperature) and 760 torr, 1 pphm is equivalent to 1·1 mPa, a 9% increase.

Based on the work reported here the ASTM Standard D-1149 has been amended (1978 version) and it now specifies expressing ozone content in accelerated chamber testing in terms of ozone partial pressure in mPa units.

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APPENDIX: INTER-LABORATORY TEST PROCEDURE

General

A special ozone 'absorption column' was used in this program in place of the 'counter-current column' as mentioned in the 1976 version of D-1149, para.

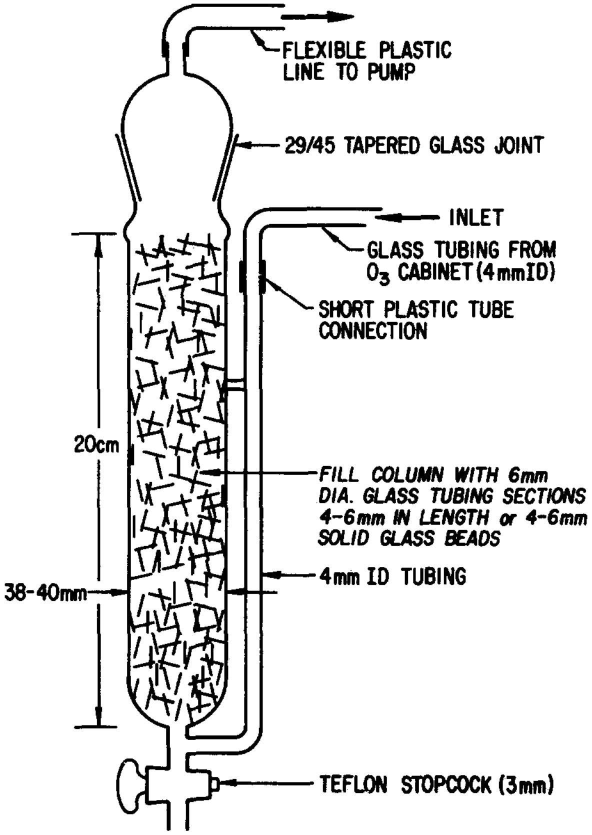

Fig. A.1. Ozone absorption column as used in inter-laboratory program.

7.2. Figure A.1 shows a schematic of this device with sufficient detail to enable a glass blower to fabricate one. Its use is outlined below. This new absorption column has been recently incorporated into D-1149.

Two identical ozone 'absorption columns' were used to conduct the ozone analysis. A common supply of KI was selected and solutions (buffer, thiosulfate) prepared at one laboratory. Portions of these were used by both laboratories. A similar titration endpoint apparatus, as described in ASTM D-1149, was used in both laboratories.

Test specimens with varying ozone resistance were prepared by one laboratory and supplied to both. These were tested for 2 and 4 h periods at three different ozone concentrations measured as per the current D-1149 ASTM procedure. Target values were 30, 50 and 70 pphm at 40 °C. Ambient atmospheric pressures during testing were recorded at both laboratories.

Test specimens

Tests were performed on bent loop specimens of 12 mm width. ASTM D-518 Method B procedure was followed except for width, as noted above, and one specimen for each test period was tested. To allow for migration of antiozonants, the test specimens were cured between aluminum foil and the foil was stripped from the specimens and they were 'conditioned' for 28 days in a dust free location without any surface strain prior to testing.

All specimens were returned to one laboratory for quantitative measurement of degree of ozone cracking. Plots of cracking v. measured ozone concentration were made for each compound and the degree of cracking at exact O_3 concentrations was scaled from the plots. The results so obtained were compared and the procedure, as outlined above, eliminated the 'variation in ozone concentration' problem that interferes with all inter-laboratory testing without standardized analysis equipment and without the special precautions taken in this program.

O_3 analysis technique

Analysis of O_3 concentration was performed after the third exposure hour at each target concentration. Current ASTM D-1149 procedure, except for modifications discussed below, was used. The procedure for using the absorption column was as follows, with reference to ASTM D-1149.

1. Flush column with distilled water.
2. Prepare KI plus buffer solution as per para. 7.2.1. Fill column to about 2/3 of total volume. Keep stopcock 3 closed.
3. Titration apparatus as specified in para. 5.1 shall be used. Reagents as specified in 6.1, 6.2, 6.3, 6.4, and 6.5.
4. After the absorption run, drain the solution in the column into a 250 ml beaker, wash down the column with 20–40 ml distilled water and collect.
5. Titrate the solution with 0·002 N thiosulfate prepared by an accurate 10 to 1 dilution of 0·02 N. Calculate the O_3 concentration according to para. 7.2.5 of D-1149.