SIMULTANEUOS EFFECT OF OZONE CONCENTRATION AND TEMPERATURE ON OZONE DEGRADATION OF RUBBER SHEETS

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The simultaneous effect of the ozone concentration and temperature on the ozone degradation has been quantitatively estimated in this paper. Dumbbell specimens of four kinds of rubber sheets capable of being stretched were subjected to five levels of ozone concentration from 10pphm (parts per hundred million) to 200pphm at 40°C. By inspecting the surfaces of the sheets periodically, it was determined that the time to failure becomes shorter with increasing ozone concentration. This relation can be expressed by the formula: $t = B / X^A$, where t is time to crack initiation or rupture (hours), X is ozone concentration (pphm), and A and B are material constants. Ozone tests were also carried out at higher temperatures such as 60°C and 80°C, indicating a rise in temperature accelerates ozone degradation. The following formula, including both parameters ozone concentration and temperature, was subsequently developed $t = 10^{(C/T + D)} / X^A$, where T is absolute temperature (K), X is ozone concentration (pphm), and A, C and D are material constants.

The same specimens were exposed outdoors in Yokohama to verify the usefulness of the formula. The ozone degradation was calculated on the assumption of some environmental conditions, and compared with the observed ones.

KEYWORDS

Degradation, estimation, formula, outdoor exposure test, ozone concentration, ozone crack, ozone test, rubber, rupture, sheet, temperature.

INTRODUCTION

It is well known that vulcanized rubber sheets applied on roofs are degraded by ozone in the atmosphere. This is especially true in sheets capable of being stretched, which may sometimes crack or rupture if they have poor ozone resistance. Although the ozone test is widely adopted as one of the important durability tests in Japan, there isn't a sufficiently clear explanation of how the process works, and of how durability may be predicted from the test. It was our purpose to connect experimental degradation to outdoor performance in order to utilize the ozone test as a durability test.

There are many factors which degrade rubber roofing sheets. In ozone degradation, the most effective factor is considered, of course, to be the concentration of ozone. But, temperature is also regarded as an important factor affecting ozone degradation. Rubber sheets are always at some variable level of temperature when they are affected by ozone. This indicates that the two factors are inseparable, and should be estimated simultaneously when determining ozone degradation.

In this paper, we studied quantitatively the effect of ozone concentration and temperature in the laboratory. We tried to develop formulas, which are based on ozone concentration and temperature, to express the time to failure. Then, the time to failure on the roof was calculated by substituting the averaged environmental data into the formulas, and the simultaneous effect of ozone and temperature was finally discussed.

SAMPLES

Vulcanized butyl rubber (IIR) sheets blended with ethylene propylene diene monomer rubber (EPDM) about 1mm thick were specially made for this study. The properties of samples against ozone were varied by changing the ratio of IIR and EPDM. The former is more sensitive to ozone than the latter. Sample codes were based on the ratio of IIR and EPDM. Table 1 shows the compositions of each sample and their fundamental physical properties obtained by tensile and hardness tests.

Each sheet was cut into dumbbell pattern No. 1 as required in JIS K 6301 and shown in Figure 1. Two test pieces were used for each test.

TEST CONDITIONS

Two kinds of tests were carried out to investigate the simultaneous effect of ozone concentration and temperature on the ozone degradation of rubber sheets.

Ozone Tests at Several Concentrations

Tests at five levels of ozone concentration including 10 ± 1pphm, 25 ± 2.5pphm, 50 ± 5pphm, 100 ± 10pphm and 200 ± 20pphm were first carried out at 40 ± 2°C to show the effect of concentration. The tests were continued until the specimens ruptured, or stopped at 1500 hours if failure had not occurred.

Ozone Tests at Higher Temperatures

Next, ozone tests were carried out at 60 ± 2°C and 80 ± 2°C to show the effect of temperature on ozone degradation. Each test was continued up to 168 hours, which is shorter than the tests previously mentioned, because ozone degradation is more severe at higher temperatures. Therefore, the time to crack initiation or rupture was expected to be shorter.

TEST PROCEDURE

Two dumbbell specimens were mounted on holders and stretched to elongations of 20, 50 and 100 percents against an initial gage length of 40mm. After being kept in an ozonefree atmosphere at 20 ± 2°C for 24 hours, the specimens were exposed to ozone in a chamber controlled at the prescribed concentration and temperature. They were periodically removed from the chamber and inspected on the surface using a magnifying glass of x10. The time to crack initiation and rupture, and the rating of cracks were recorded based on the rating method in JIS K 6301 shown in Table 2 and Photo 1.

TEST RESULTS

The test results at various levels of ozone concentration at 40°C are shown in Figure 2, and those at higher temperatures are shown in Figure 3. Fine cracks first appeared on the surfaces of specimens, became wider and deeper as the exposure time elapsed, and finally completely ruptured some specimens. The blended ratio of IIR and EPDM had a prominent affect on the ozone resistance of the specimens. An increase of EPDM improved ozone resistance. As for the patterns of ozone cracks, there are some differences among the samples as shown in Photo 2. Many smaller cracks appeared on the surface of the specimens containing little or no EPDM. In contrast, fewer but larger cracks appeared on the specimens with more EPDM.

DISCUSSIONS

Effect of Ozone Concentration

Figure 4 shows the relation between the time to crack initiation and ozone concentration. The time to crack initiation clearly became shorter as ozone concentration increased.

Figure 5 shows the relation between the time the specimens completely ruptured and the ozone concentration. In the case of all samples, except sample 50/50, the time to rupture became shorter with increasing ozone concentration. Judging from these two results, an increase of ozone concentration reduces the time to crack initiation or rupture. Or put another way, higher ozone concentration seems to give an acceleration effect to the rate of ozone degradation.

Effect of Temperature

Figure 6 shows the relation between the time to crack initiation and temperature by solid lines, and the relation of time to rupture by dotted lines. Increasing temperature reduces the time to failure for all specimens. But, the acceleration effect on ozone degradation is less than would be expected with the rise of temperature. This may possibly be explained by the formulation of a protective layer on the surface of the sheets due to the bleeding of components such as oil etc. from the rubber, and/or the larger stress relaxation induced in the specimens by higher temperatures during the tests.

FORMULA EXPRESSION OF TIME AT FAILURE

Formula Based on Ozone Concentration Alone

First, the concentration of ozone is taken into consideration to develop a formula expressing the time to crack initiation and/or rupture, because it is a basic parameter for ozone degradation of rubber sheets. The relation between the logarithmic values of time and concentration seem to have approximate linearity with each other as shown in Figures 4 and 5. This relation, then, can be expressed by the following formula:

$$t = B/X^A \qquad (1)$$

where t: time to crack initiation or rupture, hours

x: ozone concentration, pphm

A,B: constants determined from the test

The formulas obtained for each sample are shown in Table 3. The calculated results from the formulas are shown by the diagonal long- and short-dash lines for the time to crack initiation in Figure 4, and for the time to rupture in Figure 5.

Formula Composed of Both Ozone Concentration and Temperature

Next, the simultaneous effect of ozone concentration and temperature on ozone degradation is discussed. Figure 7 shows the relation between crack initiation and ozone concentration. Figure 8 shows the relation between the time to rupture and ozone concentration. It is recognized from these figures that the logarithmic values of these parameters also had approximate linearity with each other, and the ascents of the lines at 60°C and 80°C are similar to those at 40°C. This indicates that the value of A is considered to be independent of temperature and the value of B is only related to temperature.

Then, the relation between B value and temperature was investigated. Figure 9 shows the relation between them. The value of B is considered to be linear to the reciprocal of absolute temperature. Therefore, this relation can be expressed as follows:

$$B = 10^{(C/T + D)}, \qquad (2)$$

where T: absolute temperature, K

C,D: constants.

Substituting formula (2) into formula (1), the following formula is obtained:

$$t = 10^{(C/T + D)}/X^A, \qquad (3)$$

where X: ozone concentration, pphm

A,C,D: constants.

The formulas obtained for each sample to express the time to crack initiation and the time to rupture for each sample are shown in Table 4. The diagonal long- and short-dash lines in Figures 7 and 8 indicate the calculated values based on these formulas. It seems that the calculated lines are approximately in accordance with observed results.

OUTDOOR EXPOSURE TEST

Outline of the Test

To clarify the relation between the degradation indoors by the ozone tests and outdoor degradation, a two-year outdoor exposure test was carried out in Yokohama, Japan, from May 1, 1987 to April 30, 1989. The same kinds of specimens as the laboratory ozone tests were exposed in two different situations to create a temperature difference between the test pieces (i.e., in the shade and in the sun). The specimens were also stretched to an elongation of 100 percent, with half of them exposed under a screen to block the sunlight and rain, which is termed "in the shade." The other half were exposed horizontally to the zenith without a screen, termed "in the sun." Photo 3 shows the exposure situations; the left is "in the shade" and the right is "in the sun." The specimens were inspected everyday for the first month and twice a week thereafter.

Figure 10 shows the results after two years of exposure under the two situations. Both times to crack initiation and rupture became shorter in the sun than in the shade. The next reason for this difference is hypothesized; the temperature of the specimens in the sun was higher than those in the shade causing some chemical effect on the specimens in the sunlight.

Comparison of Calculated Time to Failure With Observed Data

In order to roughly estimate the degradation of rubber sheets in outdoor exposure, the time to crack initiation and the time to rupture were calculated based on the following assumptions; temperature of the specimens in the shade was 15°C which is the mean air temperature in Yokohama, temperature of the specimens in the sun was 25°C, which is 10°C higher than the air temperature, and the concentration of ozone was 3pphm which is the mean value of observed background ozone in Japan.

Substituting this averaged data into the formulas shown in Table 4, the times to crack initiation and rupture were calculated and are shown in Table 5. Although there are differences in some samples, the calculated times are similar to the observed ones. The calculated results also indicate the same tendency as the exposure tests, i.e. the time to failure in the sun is shorter than in the shade.

SUMMARY AND CONCLUSIONS

It was made clear from the various ozone tests that both an increase of ozone concentration and a rise in temperature accelerate ozone degradation. It is suggested that ozone concentration and temperature should be estimated simultaneously in the ozone test.

The time to failure can be approximately expressed by the following formula, which includes the parameters of ozone concentration and temperature:

$$t = 10^{(C/T + D)} / X^{A}.$$

The times to failure calculated by substituting the averaged temperatures and the averaged ozone concentration into the formulas, are similar to the outdoor exposure test results in Yokohama, Japan. It is concluded that the simultaneous consideration of ozone concentration and temperature is also needed for estimation of degradation of rubber sheets in outdoor applications.

ACKNOWLEDGMENTS

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Ingredients	**Sample code**			
	100/0	**80/20**	**70/30**	**50/50**
Butyl rubber (IIR)	100	80	70	50
Ethylene-propylene-diene monomer rubber (EPDM)	0	20	30	50
Zinc chloride	5	5	5	5
Stearic acid	1	1	1	1
HAF carbon black	60	60	60	60
Talc	40	40	40	40
Paraffin oil	30	30	30	30
Vulcanization accelerator (TMTD)	1	1	1	1
Vulcanization accelerator (MBT)	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5
Properties				
Thickness, mm	1.1	1.1	1.0	1.1
Tensile strength*, MPa	11.9	10.7	13.6	10.2
Elongation at break*, %	492	515	550	522
Tear strength**, MPa	3.0	2.8	3.5	2.8
Hardness***	54	52	57	54

* Dumbbell pattern No. 3 shaped test piece, elongation rate 500mm/min
** JIS B pattern shaped test piece, elongation rate 500mm/min
*** Shore durometer A

Table 1 Compositions of samples and their fundamental physical properties.

Number of cracks	**Size and depth of cracks**
A: a small number of cracks	1. That which cannot be seen with the naked eye but can be confirmed with 10 times magnifying glass.
B: a large number of cracks	2. That which can be confirmed with the naked eye.
C: numberless cracks	3. That which is deep and comparatively large (below 1mm).
	4. That which is deep and large (above 1mm and below 3mm).
	5. That which is about to crack more than 3mm or about to sever.

Table 2 Rating for the ozone cracks (JIS K 6301).

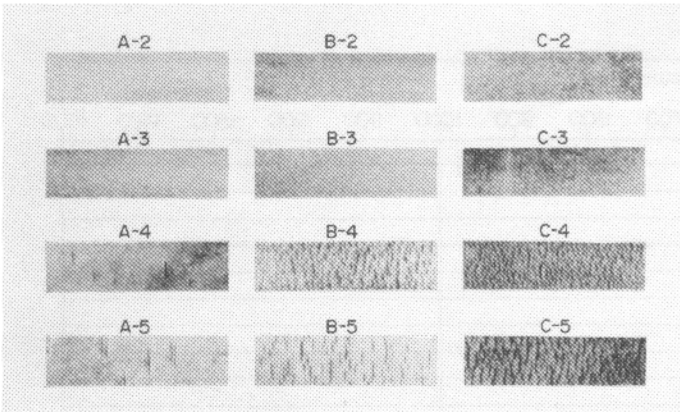

Photo 1 *Rating photographs for the ozone cracks (JIS K 6301).*

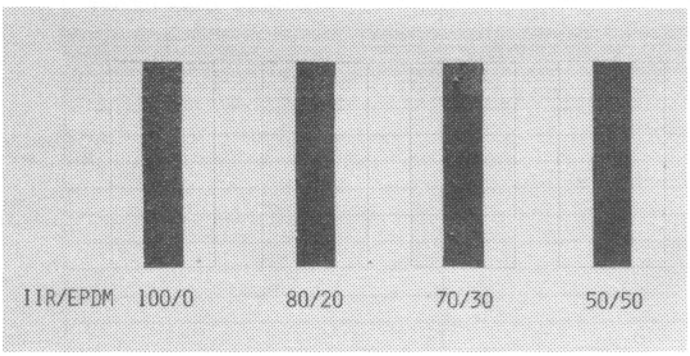

Photo 2 *Typical cracks appeared on the surfaces of specimens for each sample.*

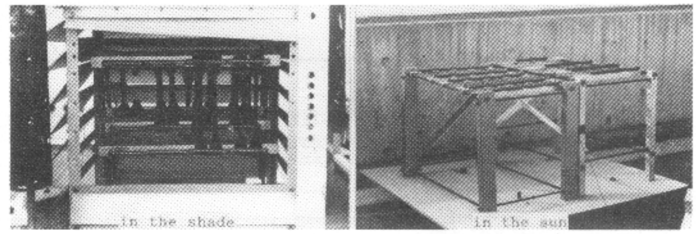

Photo 3 *Two situations of the outdoor exposure in Yokohama.*

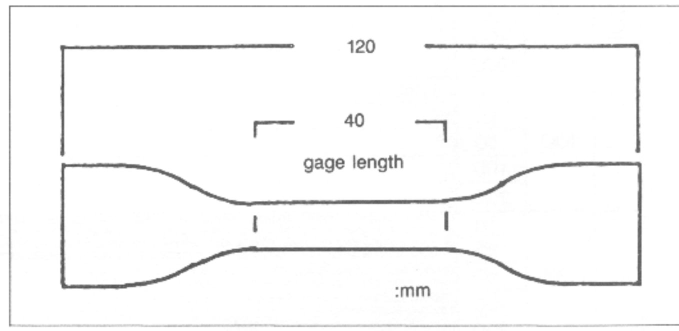

Figure 1 *Dumbbell pattern No. 1 shaped test piece.*

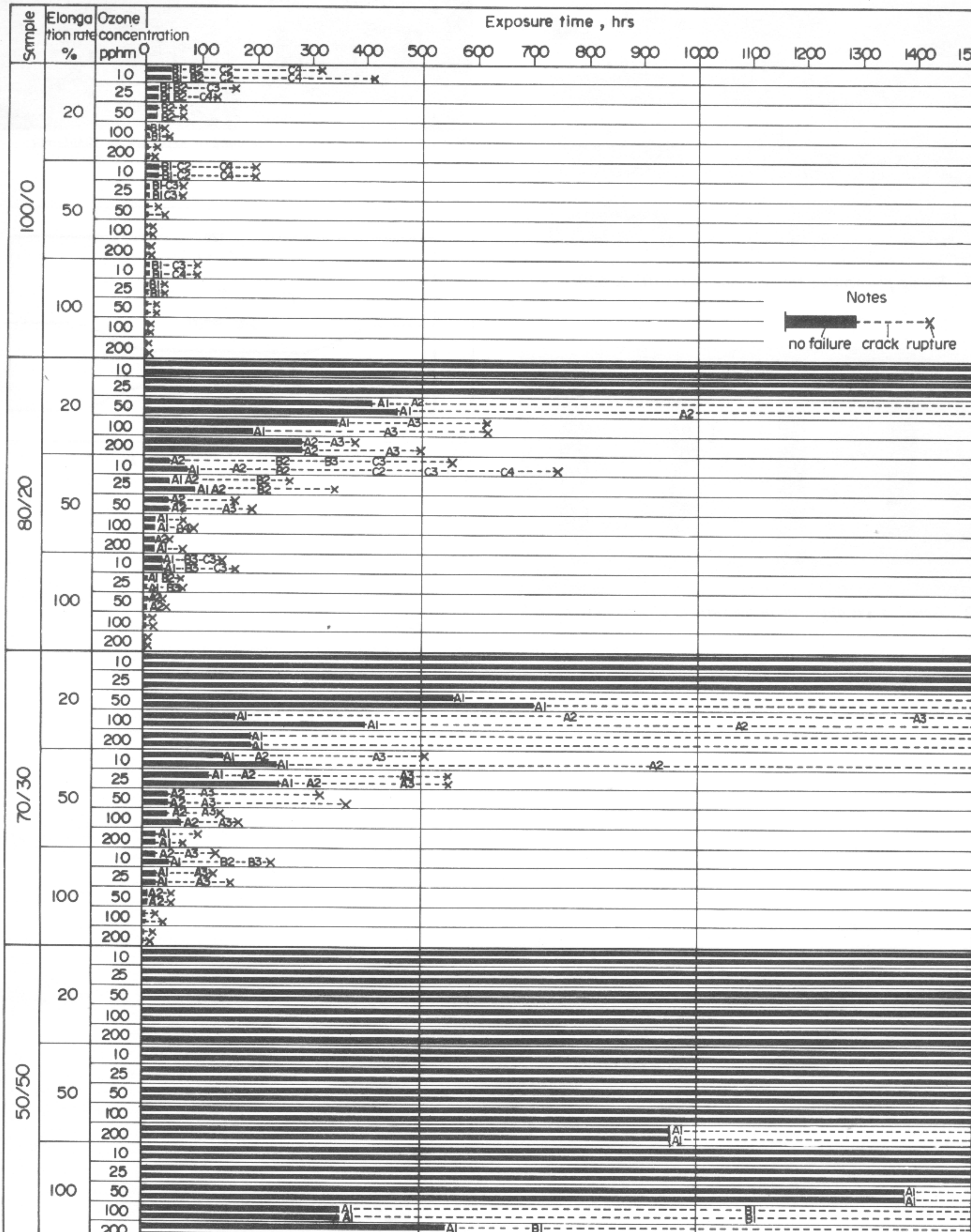

Figure 2 *Ozone test results at five levels of concentration.*

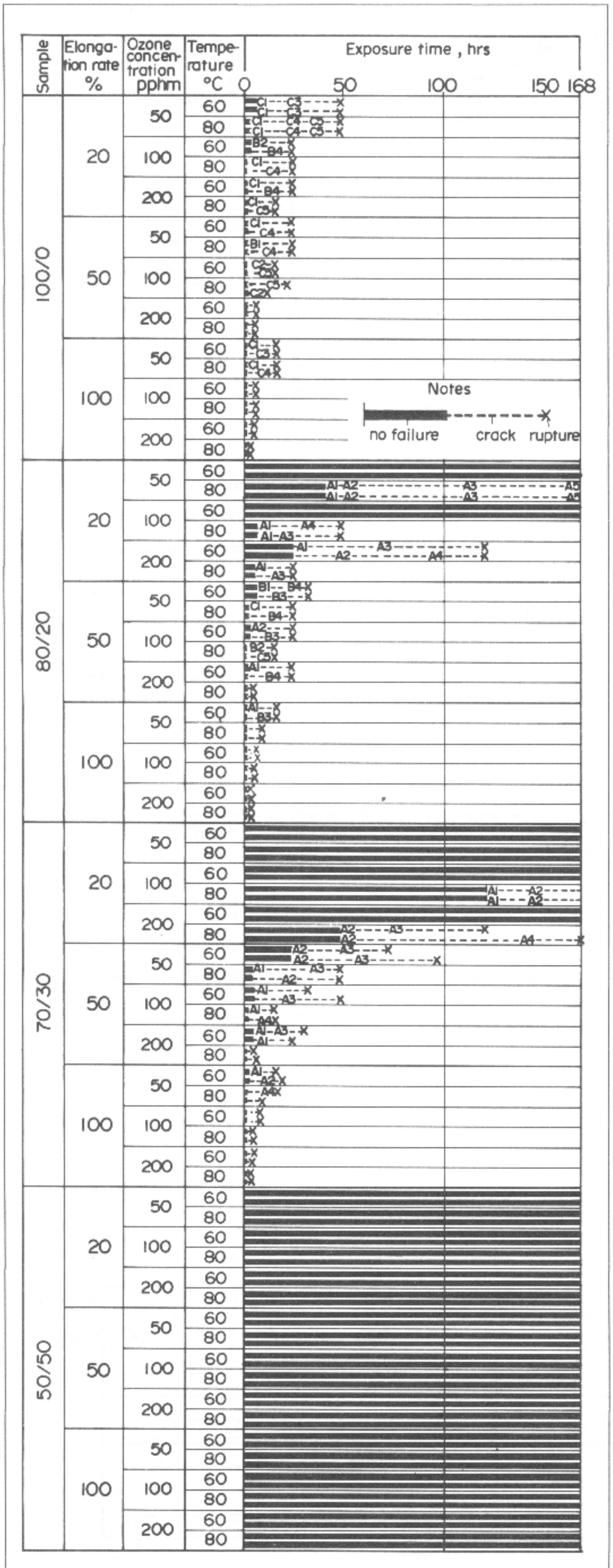

Figure 3 *Ozone test results at higher temperature.*

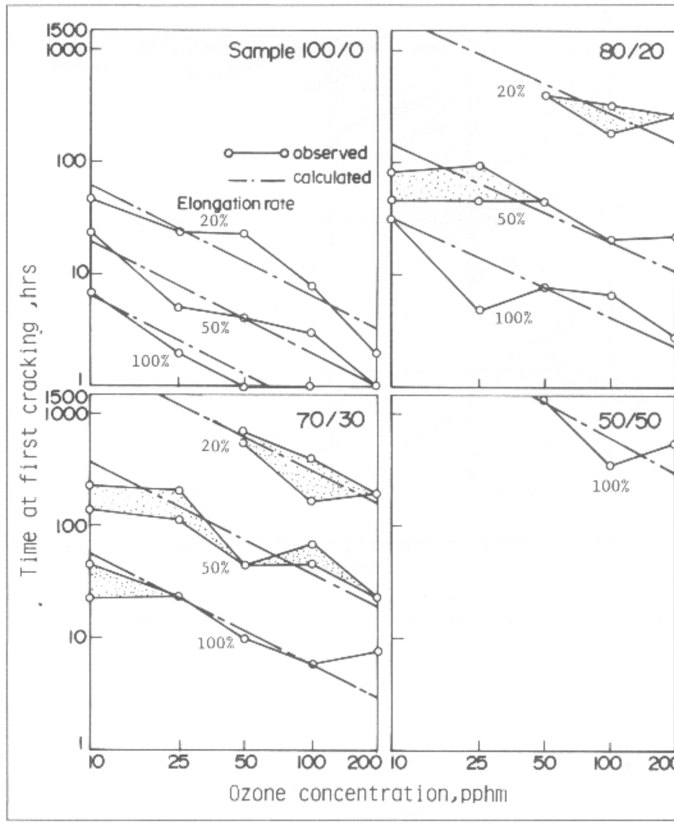

Figure 4 *Relation between the time to crack initiation and ozone concentration.*

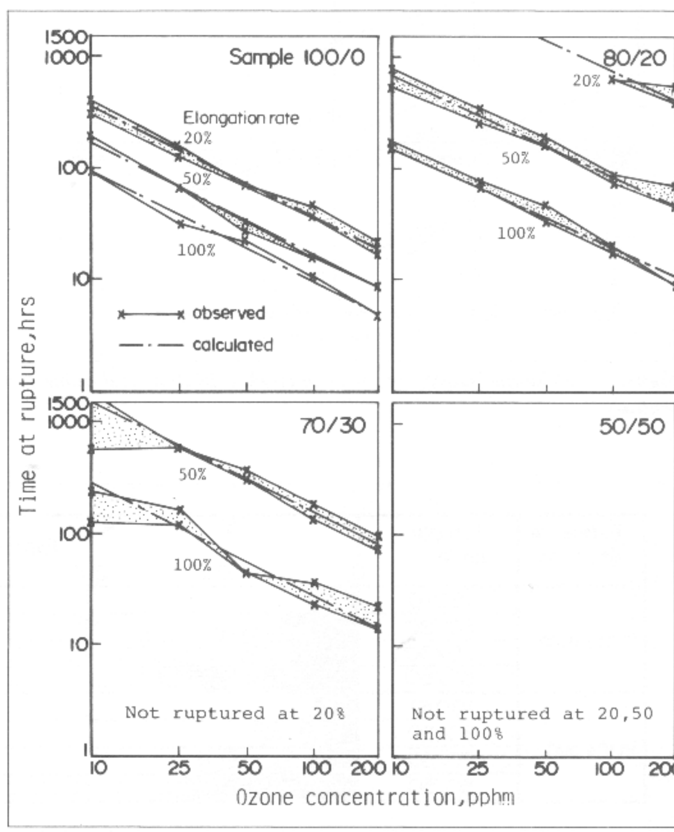

Figure 5 *Relation between the time to rupture and ozone concentration.*

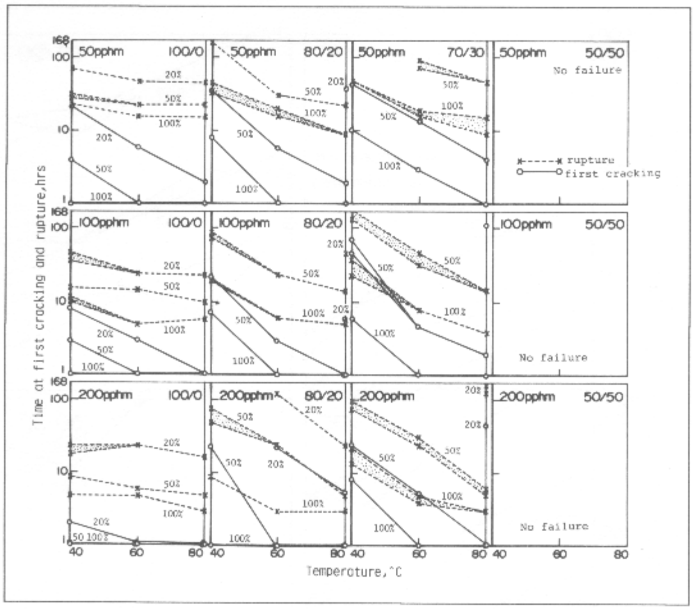

Figure 6 *Relation between the time to failure and temperature.*

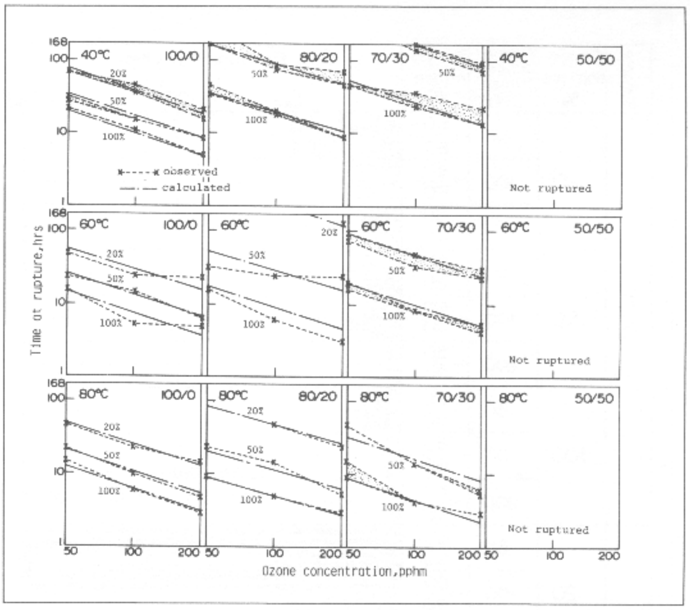

Figure 8 *Relation between the time to rupture and ozone concentration.*

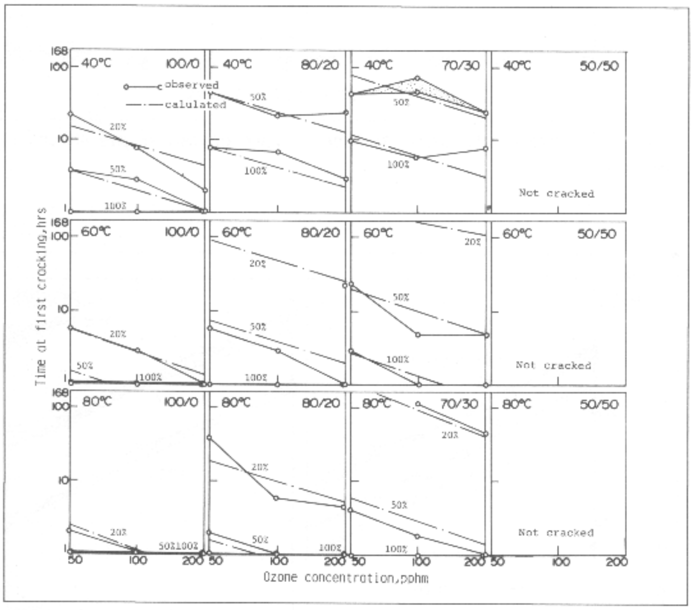

Figure 7 *Relation between the time to crack initiation and ozone concentration.*

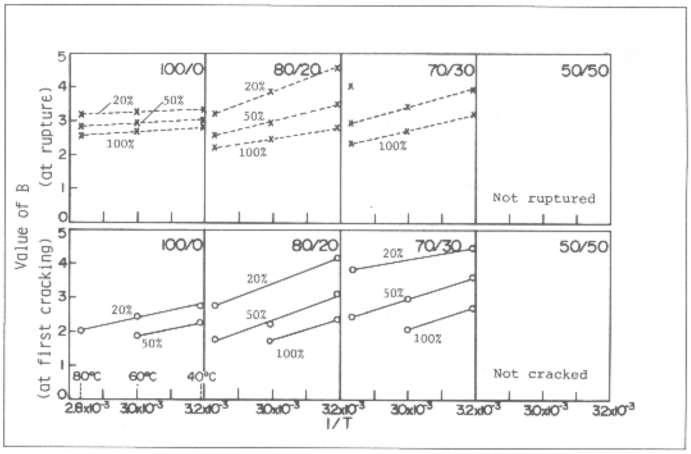

Figure 9 *Relation between logarithmic value of B and temperature.*

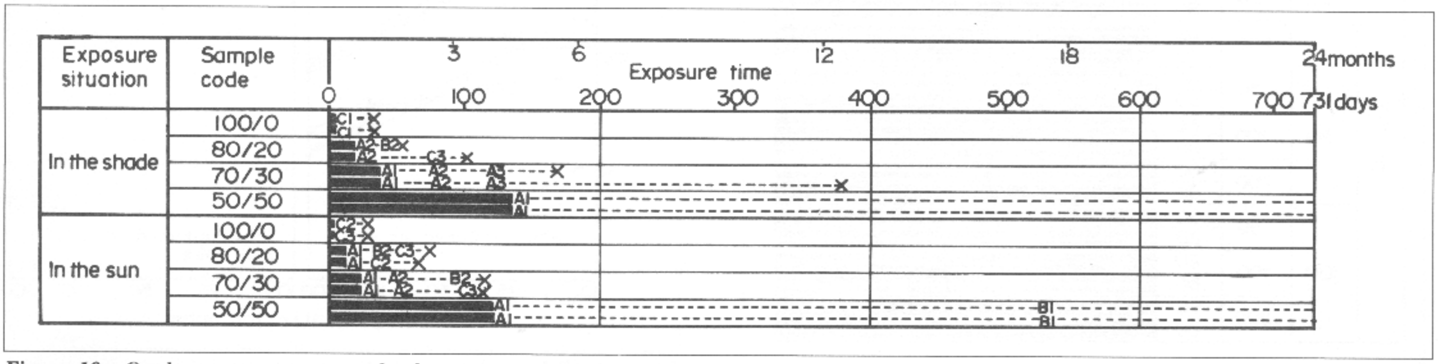

Figure 10 *Outdoor exposure test results for two years in Yokohama, Japan (at elongation rate of 100%).*