severe action on natural rubber stocks, it is used to illustrate the extreme conditions that might be caused by material migration (Figure 7 and Table IV). Two of the last three stocks contain cupric oleate in combination with various quantities and types of antioxidants. All three stocks melted when aged as a group, but when aged individually, stocks I and J showed a good retention of physical properties.

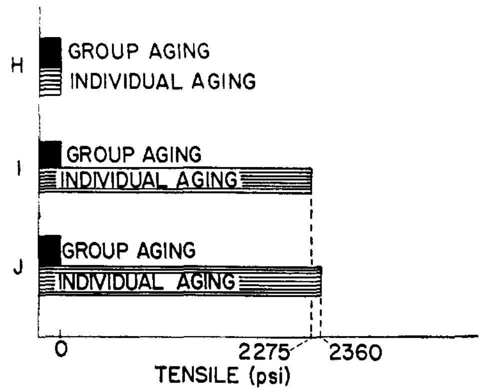

Figure 7. Effect of Migration of Cupric Oleate on Protected and Unprotected Stocks

Aged as a group and aged alone

IDENTIFICATION OF MIGRATING MATERIALS

In the early experiments, the phenomenon being studied was assumed to be migration, although no confirming data were available. In order to confirm or deny the hypothesis of migration, qualitative chemical tests were run on samples after community aging in an attempt to detect the presence of a migrating material in a stock where originally none was present.

The presence of antioxidants was confirmed by means of spot test identification (*10*). Stocks which originally contained no antioxidant showed a negative spot test, but after community aging gave positive tests for the presence of an antioxidant. This antioxidant was the same as that contained in one of the other stocks of the community group.

Quantitative sulfur determinations (*1*) were performed to confirm the migration of sulfur from one stock to another. The results obtained were sufficient only to indicate that probably sulfur moves from one stock to another. The differences in per cent sulfur obtained are small and therefore inconclusive. Additional precise testing is required.

The question of methods of avoiding migration arises. An attempt was made to prevent migration during oxygen bomb aging by placing the different stocks in individual aluminum cans with loose-fitting lids within a single bomb. Data available but unreported show that aging in these containers is equivalent to group aging, without containers, and the results are significantly different from those obtained by individual aging. It is concluded, therefore, that the use of this device is not the solution to the migration problem.

The only adequate solution appears to be aging different stocks in separate bombs. All samples contained in a bomb at a given time must be of identical composition if results are to be reliable.

SUMMARY

It has been definitely established that various materials migrate and that the magnitude of resulting test error is significant. Migration will take place whenever unlike stocks are aged together in a bomb. The most reliable test conditions prevail when separate bombs are used for individual stocks. It is recommended that specifications for oxygen bomb aging be changed. The change should specify the use of individual bombs.

ACKNOWLEDGMENT

The authors wish to express their appreciation to The Gates Rubber Co. for permission to publish this report, to Harold Thenhaus who prepared the graphs, and to other members of the staff for constructive criticism in preparation of this manuscript.

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Nondestructive Aging Tests for Rubber

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ACCELERATED aging tests have been used by the rubber industry for many years as a measure of product quality and for determining expected service life. Outdoor exposure tests have always shown poor correlation with accelerated tests because of the multiplicity of variables inherent in outdoor service conditions not met by an air oven or oxygen bomb methods.

A study of a large number of aged truck tires which had been tested in service, showed that no significant correlation of physical properties could be established between tires that failed after a few hundred miles and those that finished the 10,000-mile test run. The data showing these comparisons are given in Table I.

The conventional air-oven aging data for 7 days at 158° F. and 70 hours at 212° F. again show no correlation with natural weather aging (Table II).

Typical aging curves for natural rubber specimens which were placed outdoors for 3 years in an unstressed position and indoors on a dark shelf, show that the tensile and hardness may tend to increase at first and then decrease. The elongation loss is prob-

Table I. Service Tests on Truck Tires

Physical Property	Failure Tires	Nonfailure Tires
Tensile, av. % of orig.	83.3	74.0
Elongation, av. % of orig.	51.6	55.2
Hardness, av. points increase	8.5	3
Av. mileage	3037	10,572
No. of tires	15	10

Conventional measurements of rubber properties before and after artificial aging fail to correlate with the service life of rubber articles. Nondestructive test methods based on the change of electrical resistivity or of the strain produced by a given stress at varying time intervals on the same specimen have been devised for correlating natural aging with accelerated aging and service life.

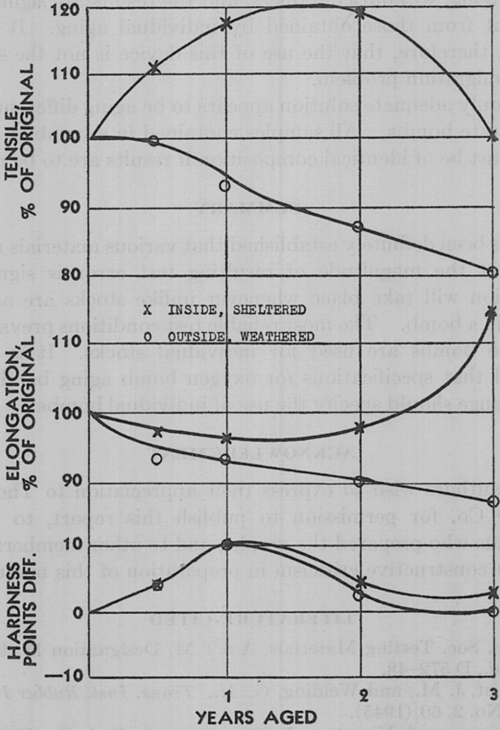

Figure 1. Changes in Physical Properties on Aging

ably the most adequate criterion of aging. Data illustrating these physical property changes are shown in Figure 1.

The deteriorating influence of ozone and sunlight on rubber is shown by the aged tire in Figure 2. Tensile, elongation, and hardness at areas removed from the cracks show no serious loss of physical properties. Therefore, it becomes imperative that an aging method be developed which will take into consideration the cracking produced by the action of ozone and sunlight.

TEST METHODS

A nondestructive rubber aging test should have good reproducibility; should be suitable for evaluating the effects of various aging media, such as heat, light, ozone, oxygen, and oils, either individually or collectively; should allow readings to be taken on the same specimen at progressive time intervals; and should express the result as a numerical quantity. Some progress in nondestructive aging tests has been made by Baxter and Roebuck (*1*) and by Tobolsky *et al.* (*4*).

ELECTRICAL RESISTIVITY METHOD

A GR-S compound containing 75 parts of acetylene carbon black per 100 parts of rubber and having a volume resistivity of 20 to 50 ohm-cm. was used for evaluating ozone cracking. T-50 specimens were cut both with and across the grain from a 0.080 inch sheet and stretched 25% in metal clamps on a plastic insulating rod. The resistance of the rubber was determined, using a Wheatstone bridge.

The apparatus is shown in Figure 3. As the cracks develop in the specimen, the cross-sectional area is reduced and the volume resistivity increases. As many cracks are formed, the resistance reading is dependent on the crack producing the greatest reduction in area or the greatest penetration.

The data obtained from samples exposed to an ozone concentration of 0.015% at 100° F. are shown in Figure 4. The specimens were cracked sufficiently to break in the region of 30,000 ohms. The difference in the curves illustrates the effect of the grain, causing a higher resistance in one direction.

Table II. Air-Oven Aging *vs.* Weather Aging of Tire Tread Stocks

Aging Condition	Tensile, % Retention	Elongation, % Retention	Hardness, Points Increase
Air oven, 7 days at 158° F.	107	76	6
Air oven, 70 hours at 212° F.	92	53	10
Weather, 5 years	82	50	10

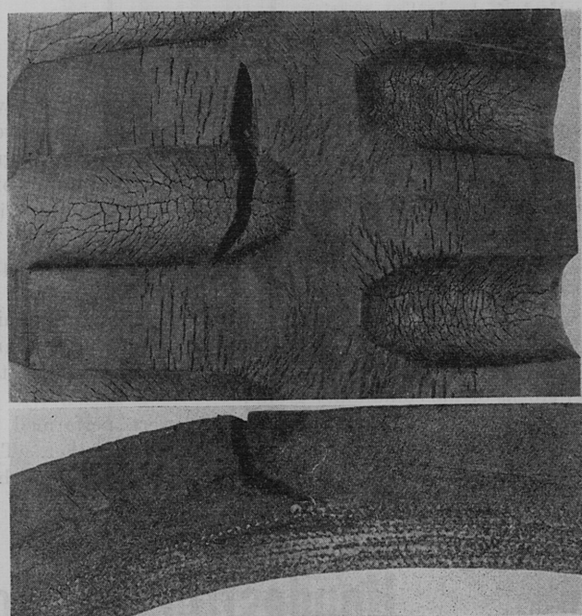

Figure 2. Effect of Ozone and Sunlight

Upper. Tread view
Lower. Section view

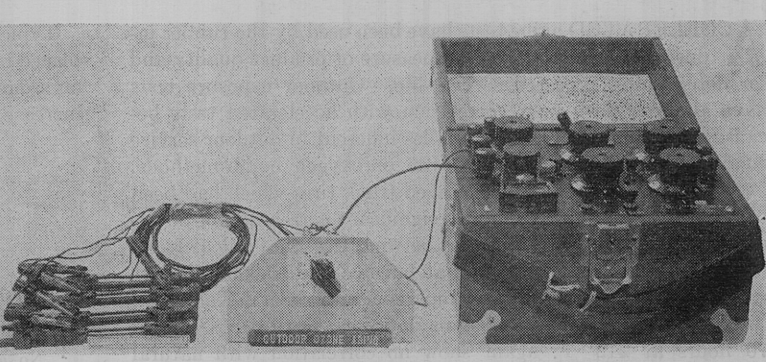

Figure 3. Apparatus for Electrical Resistivity Method

Tests made outdoors and proceeding under atmospheric ozone conditions gave similarly shaped curves but were not reproducible. This may be attributed to variations in ozone concentration, temperature difference, and the influence of moisture.

REVERSE MODULUS METHOD

The increase in elongation of a T-50 specimen caused by the application of a constant load to the stretched specimen at various time intervals was used to measure the amount of ozone cracking. The test apparatus, shown in Figure 5, is a permanent set apparatus mounted in a vertical position. The specimens are stretched 25% and clamped at that extension. After exposure to ozone, the clamps are loosened, a 400-gram load is hung on the lower clamp, and the resulting elongation is measured. Typical data for such a test are shown in Figure 6. As the cracks develop, the constant load causes an increase in elongation, thereby producing a measurable quantity.

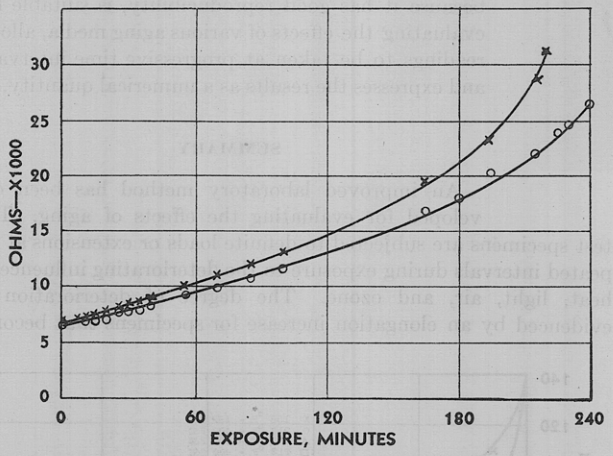

Figure 4. Effect of Exposure to Ozone Concentration

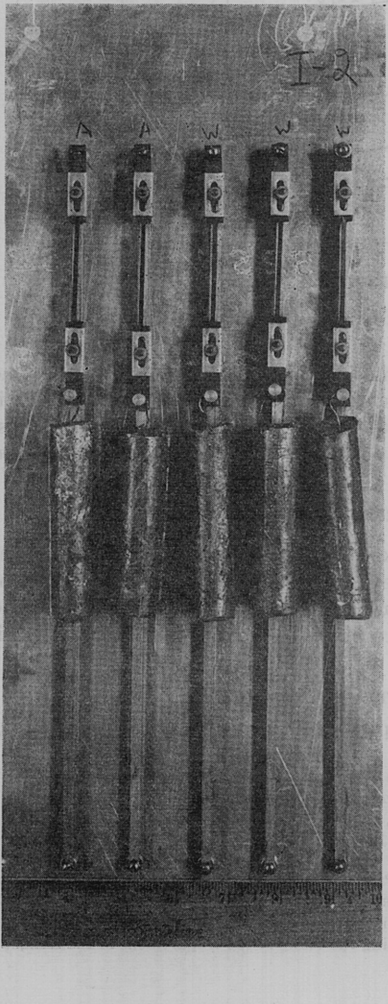

Figure 5. Test Apparatus for Reverse Modulus Method

STRAIN TEST METHOD

In view of the potentialities of the reverse modulus method, it was decided to investigate a more sensitive apparatus called the "strain tester for rubber." A picture of the apparatus is shown in Figure 7. The details of construction (*2*) and the method of operation have been described (*3*). The apparatus is well suited for determining the elongations caused by loadings at 100, 200, and 400 pounds per square inch. These elongations are high enough for good sensitivity and reproducibility, but not so high

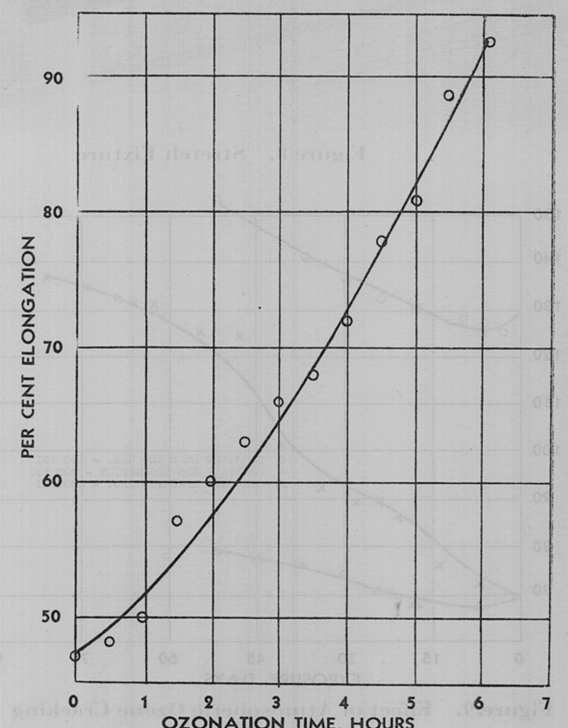

Figure 6. Ozone Cracking

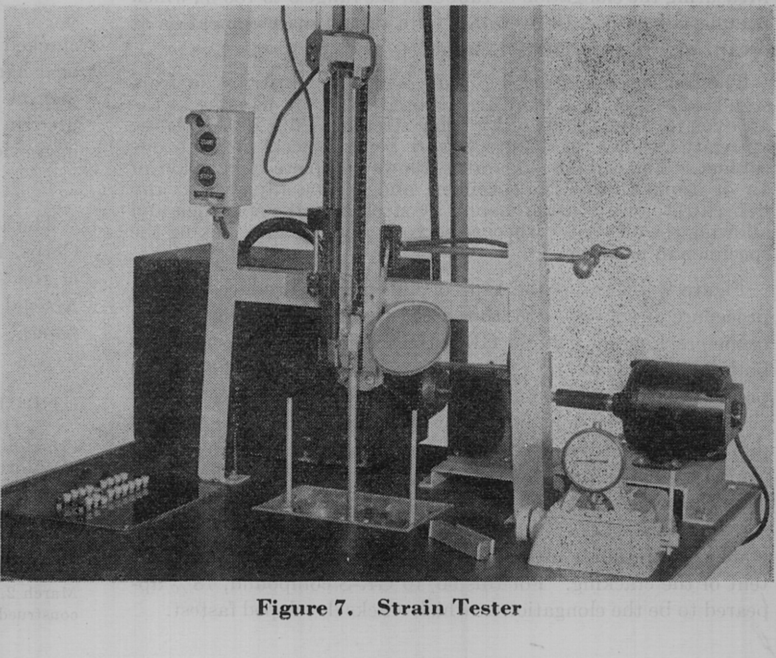

Figure 7. Strain Tester

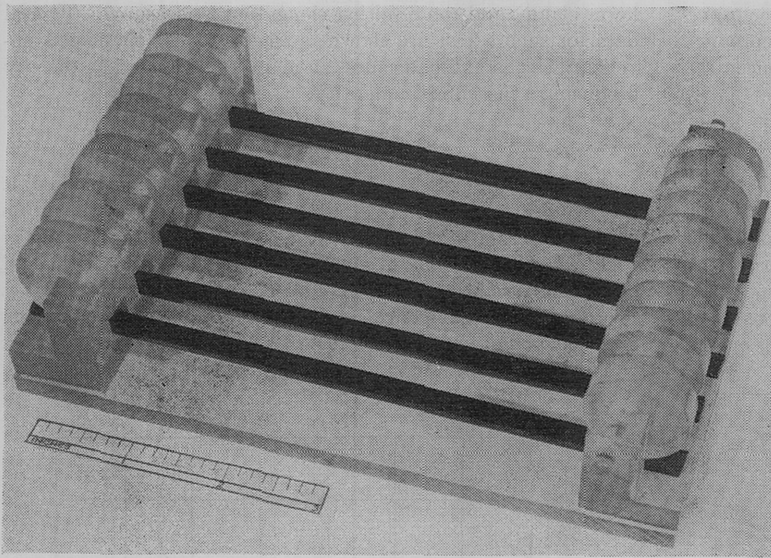

Figure 8. Stretch Fixture

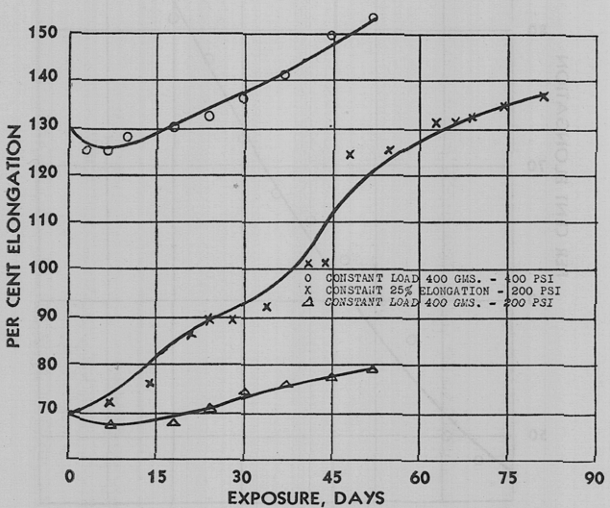

Figure 9. Effect of Atmospheric Ozone Cracking

as to cause adverse effects such as permanent set or tearing. Measuring the elongation of rubber in the range 0 to 150%, which includes all service usage, rather than the ultimate elongation at break, appears to be most desirable.

The test specimens are 6 × 0.25 × 0.080 inch strips cut from standard test pads. They are exposed either by hanging in the air oven for heat effects or by being stretched 25% in the plastic apparatus shown in Figure 8 and being placed in an ozone cabinet. The stretch apparatus allows complete circulation of air or ozone around the specimen, and can be adjusted to any desired rate of extension merely by stretching the specimen and allowing the off-center wheel to serve as a wedge grip locking the specimen in position.

Figure 9 illustrates the type of information produced by the procedure described. In this case, the effect of atmospheric ozone cracking on a 90/10 GR-S tread composition is shown for both constant load and constant elongation at either 200 or 400 pounds per square inch measuring load on the strain tester.

The increase in slope of the constant elongation curve may be due to increased outdoor ozone concentrations. The decreased slope may indicate that cracking had developed to such a point that the stress was relieved somewhat and the cracking rate slowed down. Other tests have shown that the rate of ozone cracking is a function of the per cent elongation, not of the extent of the cracking. For this 90/10 GR-S compound, 18% appeared to be the elongation at which cracks developed fastest.

The effects of conventional circulating air-oven aging tests are shown in Figure 10. These decreased elongations or modulus increases with time are in contrast to the increased elongations observed in the ozone tests. Measurements were made at both 158° and 212° F. and at both 200 and 400 pounds per square inch loadings. The tests, which were run up to 60 days, show that the greatest loss in elongation occurs during the first 10 days.

The loss in elongation is probably the greatest factor in the failure of rubber items, as evidenced by both artificial and natural aging methods.

It is felt that the strain test method meets the requirements of a nondestructive rubber aging test, because it has good reproducibility, is suitable for evaluating the effects of various aging media, allows readings to be taken at progressive time intervals, and expresses the results as a numerical quantity.

SUMMARY

An improved laboratory method has been developed for evaluating the effects of aging. The test specimens are subjected to definite loads or extensions at repeated intervals during exposure to the deteriorating influence of heat, light, air, and ozone. The degree of deterioration is evidenced by an elongation increase for specimens that become cracked and for a decrease in elongation for those that become heat-hardened. The test data are obtained on the same specimen at varying time intervals, are reproducible, and are measured in the low elongation range in which most rubber is used in service.

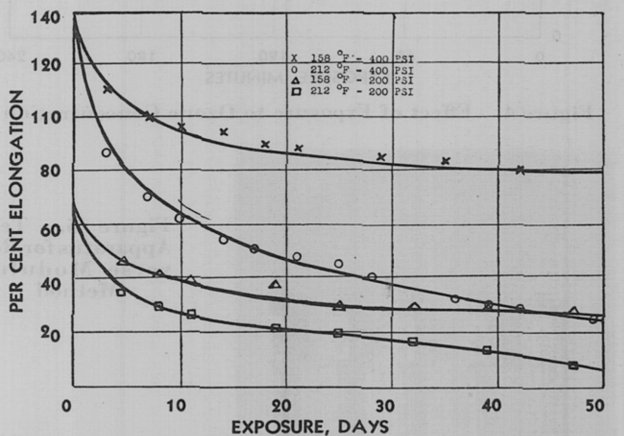

Figure 10. Effect of Circulating Air-Oven Aging Tests

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