An Apparatus for Quantitative Gas-Absorption Measurements

J. REID SHELTON and E. T. MCDONEL

Department of Chemistry and Chemical Engineering, Case Institute of Technology, Cleveland 6, Ohio

INTRODUCTION

A research program devoted to a study of the factors involved in the oxidative aging and deterioration of natural and synthetic rubber polymers and vulcanizates has been in progress in this laboratory for a number of years. To accomplish this work the volumetric method of measuring oxygen absorption by volume change at constant temperature and pressure was adopted. This method was selected on the basis that it is more convenient and reliable than such other procedures as gravimetric or manometric methods. Volumetric oxygen absorption is subject to less variation than aging studies based on physical property measurements, and the rate of oxidation is not masked by the effect of variations in compounding upon changes in physical properties.

The apparatus initially assembled for volumetric oxygen absorption was adapted from Kohman[1] and has been fully described by Shelton and Winn.[2] This unit was significantly improved by substituting an aluminum block for the oil bath as a source of heat at constant temperature, as described in detail by Blum, Shelton, and Winn.[3] A recent adaptation of a commercially-produced aluminum aging block has resulted in a volumetric gas absorption unit with performance superior to that of previous units.

EQUIPMENT

The constant temperature section consists of a modification of a Scott Tester's standard model LG aluminum aging block heating bath, 15 inches high, 25 inches in diameter, and weighing about 400 pounds. The block contains 28 holes, approximately 12 inches deep (including insulation) and $1^1/_2$ inches in diameter, for inserting sample tubes. Fourteen holes are located on a $5^1/_2$-inch radius from the center and fourteen holes are located on a $7^1/_2$-inch radius. The unit was modified to hold sample tubes with ground glass joints by counterboring the outer row of fourteen holes $1^3/_8$ inches into the aluminum block ($3^3/_8$ inches including insulation) and two inches in diameter. Four 1000-watt strip heaters on the circumference of the block and a Fenwal thermoregulator provide maximum temperatures in the range of 290°C. and control within ±0.25°C.

The commercial aging block, after modification as described above, was mounted within an octagonal-shaped carriage with the control panel utilizing one side of the octagon, as may be seen in Figure 1. On each of the seven remaining sides are mounted two water-jacketed burets and two stainless steel rods as runners for the leveling bulb clamps. The burets are held to the frame by

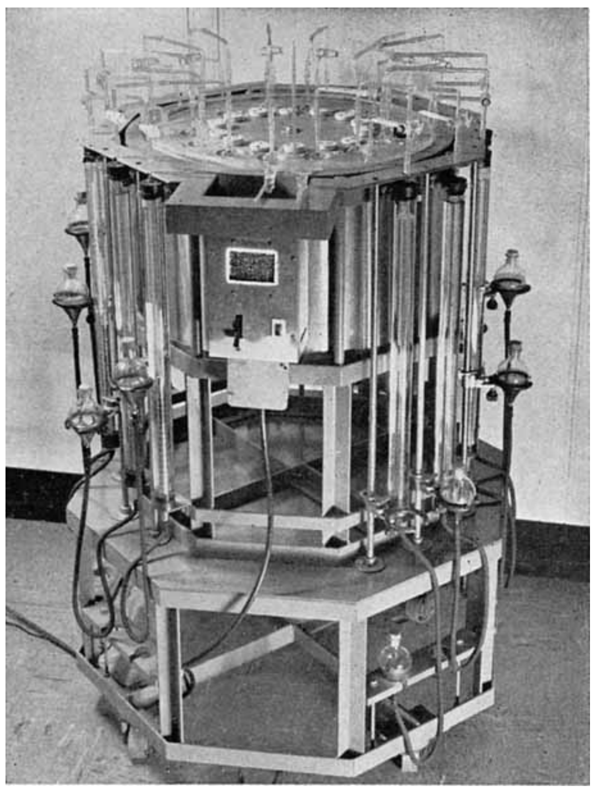

Fig. 1. Front view of volumetric gas-absorption apparatus.

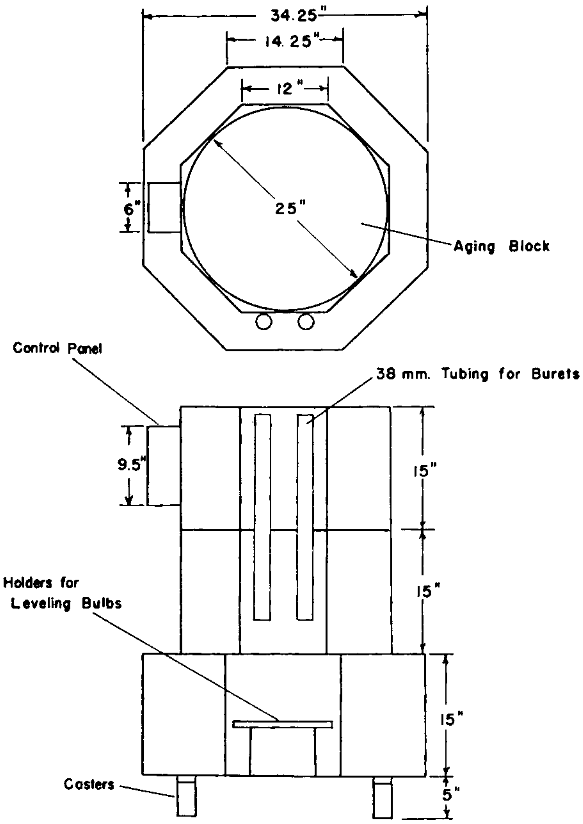

Fig. 2. Schematic diagram of the top and side views of the assembled unit and carriage.

ordinary broom clamps to facilitate easy dismantling for cleaning. The burets are connected to the sample tubes through three-way stopcocks which also join to a manifold on the top of the unit

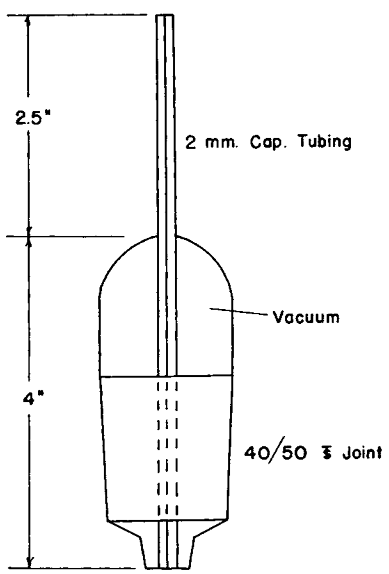

Fig 3. Evacuated cap for sample tubes.

for evacuating and filling the sample tubes. Short sections of Tygon tubing are used to seal these connections.

The frame is constructed of $1^1/_2 \times 1^1/_2 \times {}^1/_4$-inch angle iron and is mounted on four truck casters for easy moving. Funnel support arms are mounted on the lower part of the frame for holding the leveling bulbs when not in use or when evacuating the sample tubes. The overall height of 50 inches makes the unit low enough for easy loading from the top. A schematic diagram of the unit may be seen in Figure 2.

The sample tubes are ten inches long and the upper ends are made from 40/50 ground glass joints. Selected nominal 38-mm. o.d. Pyrex tubing is used to make the sample tube walls. This diameter gives a snug fit in the aging block holes. The caps are made from 40/50 inner members with drip tips. A 2-mm. capillary tubing is sealed through the center of the cap as shown in Figure 3. The space surrounding the capillary tubing is evacuated and permanently sealed. This vacuum seal reduces convection cooling from the top and gives much better temperature distribution within the sample tube than does the ordinary open cap.

DISCUSSION

The procedure in operating this type of apparatus has been adequately described in previous publications.[2–4] Table I shows the temperature distribution measured along the center line of a sample tube at various points between the top and bottom. This distribution is essentially constant over most of the tube, and excellent uniformity of temperature is shown in the lower five-inch section which contains the sample. The heating rates of sample tubes after placement in the aluminum block at a given temperature are shown in Table II. These data are representative of all fourteen holes tested and showed very little variation among holes. Essentially constant temperature is attained within 6 minutes when the block is already at 150°C., while somewhat longer times are required at lower block temperatures. The heating rates of this unit are superior to those of earlier versions of this apparatus that have been used in this laboratory. This rapid heatup is of extreme importance when the unit is used, for example, as an oven in the kinetic study of vulcanizations. If it is necessary to start volume measurements before temperature equilibrium is established, control tubes containing the appropriate gas but no sample may be intro-

TABLE I
Temperature Distribution at Various Levels in Sample Tube, Block Temperature 150.5°C.

Height from bottom of tube, in.	Temperature, °C.
0	150.0
1	150.0
2	150.5
3	150.5
4	150.5
5	150.5
6	149.0
7[a]	142.0

[a] At cap

TABLE II
Rate of Sample Tube Heatup, on Center Line of Tube 3 Inches from Bottom Ambient Temperature 23°C.

Time after introduction, min.	Tube temperature, °C. (block temp. 150°C.)	Tube temperature, °C. (block temp. 110°C.)
0.5	57.5	54.0
1.0	93.5	71.0
1.5	113.0	—
2.0	124.0	79.0
3.0	138.0	89.0
4.0	143.5	93.5
5.0	147.5	98.0
6.0	149.0	—
7.0	149.5	104.5
10.0	149.5	108.0
12.0	—	109.5
15.0	—	110.0

duced simultaneously to provide a correction for volume changes due to temperature variation.

Volumetric gas-absorption units have been used in this laboratory primarily for studies of the oxidation of rubber.[5–7] However, the versatility of the apparatus is such that it lends itself to the study of a variety of materials at controlled temperatures under controlled gaseous atmospheres. The unit is arranged to allow the isolation of test samples so that individual samples may be removed at various times. The apparatus has also been used in this laboratory to study the oxidation of polyethylene[8,9] and expoxide coatings.[10] Presently, the volumetric oxygen-absorption technique is being used to measure the effectiveness of drying oils for paints. The units have also been used for the curing of polyurethanes under moisture-free conditions and for the vulcanization of rubber under nitrogen.

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Synopsis

An apparatus for quantitative gas-absorption measurements is described and illustrated with drawings and photograph. A commercially available aluminum block heating unit, adapted to accommodate glass sample tubes, is mounted in an octagonal frame. Gas burets and leveling bulbs are supported on the frame to provide an apparatus for measuring volume changes at a given pressure. Data on rate of heatup and temperature distribution within a sample tube are given. The apparatus has been used primarily for volumetric oxygen-absorption measurements in studies related to the oxidation of rubber, but it is adaptable to studies involving other materials and other gaseous atmospheres at controlled temperatures. For example, studies have been made with polyethylene, epoxide coatings, and drying oils. The apparatus has also proved useful for curing polyurethanes under moisture-free conditions and for the vulcanization of rubber in a nitrogen atmosphere.

Résumé

Un appareil pour les mesures quantitatives d'absorption gazeuse est décrit et illustré par des dessins et une photographie. Un bloc chauffant en aluminium, apte à contenir des tubes en verre à échantillon, est monté sur un support octagonal. Des burettes à gaz et des boules à niveau sont portés par le support de façon à pouvoir mesurer les variations de volume à une pression donnée. Des données sur la vitesse de chauffage et sur la distribution de la température au sein d'un tube à échantillon sont indiquées. L'appareil a été utilisé au début pour des mesures volumétriques d'absorption d'oxygène dans des études d'oxydation du caoutchouc mais il est applicable aux études sur d'autres matériaux, et d'autres atmosphères gazeuses à des températures controlées. Par exemple, des études ont été faites avec le polyéthylène, des revêtements époxydiques et des huiles siceatives. L'appareil est également utilisable au post-traitement des polyurethanes à l'abri de l'humidité et à la vulcanisation du caoutchouc sous une atmosphère d'azote.

Zusammenfassung

Ein Apparat zur quantitativen Messung der Gasabsorption wird beschrieben und die Beschreibung durch Skizzen und ein Lichtbild ergänzt. Eine im Handel erhältliche Aluminiumblock-Heizeinrichtung, die zur Aufnahme von Glasproberöhren eingerichtet wurde, wird in einem achteckigen Rahmen montiert. Gasbüretten und Niveaugefässe werden an dem Rahmen angebracht, so dass mit dem Apparat Volums-änderungen bei gegebenem Druck gemessen werden können. Zahlen für die Aufheizgeschwindigkiet und die Temperaturverteilung innerhalb einer Proberöhre werden angegeben. Die Apparatur wurde zunächst für volumetrische Sauerstoffabsorptionsmesungen bei der Untersuchung der Oxydation von Kautschuk verwendet; sie kann aber für Untersuchungen an anderen Materialien und mit anderen Gasatmosphären unter Temperaturkontrolle adaptiert werden. So wurden z.B. Untersuchungen mit Polyäthylen, Epoxydüberzügen und trocknenden Ölen durchgeführt. Die Apparatur erwies sich auch für die Nachbehandlung von Polyurethanen unter Feuchtigkeitsausschluss, sowie für die Vulkanisation von Kautschuk in einer Stickstoffatmosphäre als brauchbar.

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