Designation: G91 – 11

Standard Practice for
Monitoring Atmospheric SO_2 Deposition Rate for Atmospheric Corrosivity Evaluation[1]

This standard is issued under the fixed designation G91; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers two methods of monitoring atmospheric sulfur dioxide, SO_2 deposition rates with specific application for estimating or evaluating atmospheric corrosivity as it applies to metals commonly used in buildings, structures, vehicles and devices used in outdoor locations.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D516 Test Method for Sulfate Ion in Water
D1193 Specification for Reagent Water
D2010/D2010M Test Methods for Evaluation of Total Sulfation Activity in the Atmosphere by the Lead Dioxide Technique
G16 Guide for Applying Statistics to Analysis of Corrosion Data
G84 Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing
G140 Test Method for Determining Atmospheric Chloride Deposition Rate by Wet Candle Method
G193 Terminology and Acronyms Relating to Corrosion

2.2 *ISO Standards:*[3]

ISO 9225 Corrosion of metals and alloys- Corrosivity of atmospheres – Measurement of environmental parameters affecting corrosivity of atmospheres

3. Terminology

3.1 *Definitions*—The terminology used herein shall be in accordance with Terminology and Acronyms G193.

4. Summary of Practice

4.1 Sulfation plates consisting of a lead peroxide reagent in an inverted dish are exposed for 30-day intervals. The plates are recovered and sulfate analyses performed on the contents to determine the extent of sulfur capture. Lead peroxide cylinders are also used for monitoring atmospheric SO_2 in a similar manner. The results are reported in terms of milligrams of SO_2 per square metre per day.

5. Significance and Use

5.1 Atmospheric corrosion of metallic materials is a function of many weather and atmospheric variables. The effect of specific corrodants, such as sulfur dioxide, can accelerate the atmospheric corrosion of metals significantly. It is important to have information available for the level of atmospheric SO_2 when many metals are exposed to the atmosphere in order to determine their susceptibility to corrosion damage during their life time in the atmosphere.

5.2 Volumetric analysis of atmospheric SO_2 concentration carried out on a continuous basis is considered by some investigators as the most reliable method of estimating the effects caused by this gas. However, these methods require sophisticated monitoring devices together with power supplies and other equipment that make them unsuitable for many exposure sites. These methods are beyond the scope of this practice.

5.3 The sulfation plate method provides a simple technique to independently monitor the level of SO_2 in the atmosphere to yield a weighted average result. The lead peroxide cylinder is

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[1] This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.04 on Atmospheric Corrosion.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

similar technique that produces comparable results, and the results are more sensitive to low levels of SO_2.

5.4 Sulfation plate or lead peroxide cylinder results may be used to characterize atmospheric corrosion test sites regarding the effective average level of SO_2 in the atmosphere at these locations.

5.5 Either sulfation plate or lead peroxide cylinder testing is useful in determining microclimate, seasonal, and long term variations in the effective average level of SO_2.

5.6 The results of these sulfur dioxide deposition rate tests may be used in correlations of atmospheric corrosion rates with atmospheric data to determine the sensitivity of the corrosion rate to SO_2 level.

5.7 The sulfur dioxide monitoring methods may also be used with other methods, such as Practice G84 for measuring time of wetness and Test Method G140 for atmospheric chloride deposition, to characterize the atmosphere at sites where buildings or other construction is planned in order to determine the extent of protective measures required for metallic materials.

6. Interferences

6.1 The lead peroxide reagent used in the sulfation plates or lead peroxide cylinders may convert other sulfur containing compounds such as mercaptans, hydrogen sulfide, and carbonyl sulfide into sulfate.

NOTE 1—Hydrogen sulfide and mercaptans, at concentrations which affect the corrosion of structural metals significantly, are relatively rare in most atmospheric environments, but their effects regarding the corrosion of metals are not equivalent to sulfur dioxide. Therefore, if H_2S, COS, or mercaptans are present in the atmosphere, that is, the odor of rotten eggs is present, the lead peroxide method must not be used to assess atmospheric corrosivity. It should also be noted that no actual measurements have been made which would establish the correlation between atmospheric H_2S, COS, or mercaptan level and sulfation as measured by this practice.

6.2 The inverted exposure position of the sulfation plate is intended to minimize capture of sulfuric acid aerosols and sulfur bearing species from precipitation. The lead peroxide cylinder method may be more susceptible to capturing sulfuric acid aerosol particles. However, it should be noted that such aerosols are rare in most natural environments.

7. Preparation of SO_2 Deposition Monitoring Devices

7.1 Sulfation plates can be prepared according to the method of Huey.[4] The plate preparation method is given in Appendix X1. Laboratory prepared plates should be exposed within 120 days of preparation.

7.2 Lead peroxide cylinders can be prepared as shown in ISO 9225. The cylinder preparation procedure is also shown in Appendix X2. Lead peroxide cylinders should be exposed within 120 days of their preparation, and if stored they should be kept in a cool dry location.

8. Exposure of SO_2 Monitoring Devices

8.1 In general, the level of atmospheric sulfur dioxide varies seasonally during the year so that a minimal exposure program requires four 30-day exposures each year at roughly equal intervals. In order to establish the atmospheric SO_2 level at an atmospheric corrosion test site which has not been monitored previously, a program in which six 30-day exposures per year for a period of 3 years is recommended. More extensive testing may be desirable if large variability is encountered in the results. Thereafter, the location should be monitored with at least four tests in a 1-year period every 3 years. If the subsequent tests are not consistent with the initial testing, then another 3-year program of six tests per year is required. Also, if a major change in the general area occurs in terms of industrial or urban development, then six tests per year for 3 years should again be carried out.

8.2 In monitoring exposure sites, a minimum of four plates or two cylinders shall be used for each exposure period.

8.2.1 Sites which have a significant grade or elevation variation should be monitored with at least two plates or one cylinder at the highest elevation and two plates or one cylinder at the lowest elevation.

8.2.2 Plates and cylinders should be exposed, if possible, at both the highest and lowest level above the ground at which corrosion test specimens are exposed.

8.2.3 Sites larger than 10 000 m^2 shall have at least eight plates or four cylinders exposed for each period. In rectangular sites on level ground, it is desirable to expose two plates or one cylinder at each corner.

NOTE 2—Some investigators have reported significantly higher sulfation results at locations closest to the ground.

8.3 *Installation:*

8.3.1 Brackets shall be used to hold the sulfation plates securely in an inverted position so that the lead peroxide mixture faces downward. The plate shall be horizontal and shall be placed so that it is not protected from normal winds and air currents. The bracket design should include a retaining clip or other provision to hold the plate in the event of strong winds. The retainer clip may be made from stainless steel, spring bronze, hard aluminum alloy (3003H19), or other alloys with sufficient strength and atmospheric corrosion resistance. A typical bracket design is shown in Fig. 1.

8.3.2 For lead peroxide cylinders, each device shall be exposed in a support similar to that shown in Test Method G140 for chloride candles. Each cylinder shall be securely mounted in a vertical position with a clamp or other device to hold it securely against wind or other mechanical forces. A cover at least 300 mm in diameter shall be securely mounted above each cylinder with a clearance of 200 mm between the top on the cylinder and the bottom of the cover. The cover may also be rectangular or square with a minimum size of 300 mm for the smallest dimension. The stand and cover assembly should be constructed of materials that are not degraded by atmospheric exposure for the expected duration of their service.

8.4 A 30 ± 2-day exposure period is recommended for either the plates or cylinders. At the conclusion of this period,

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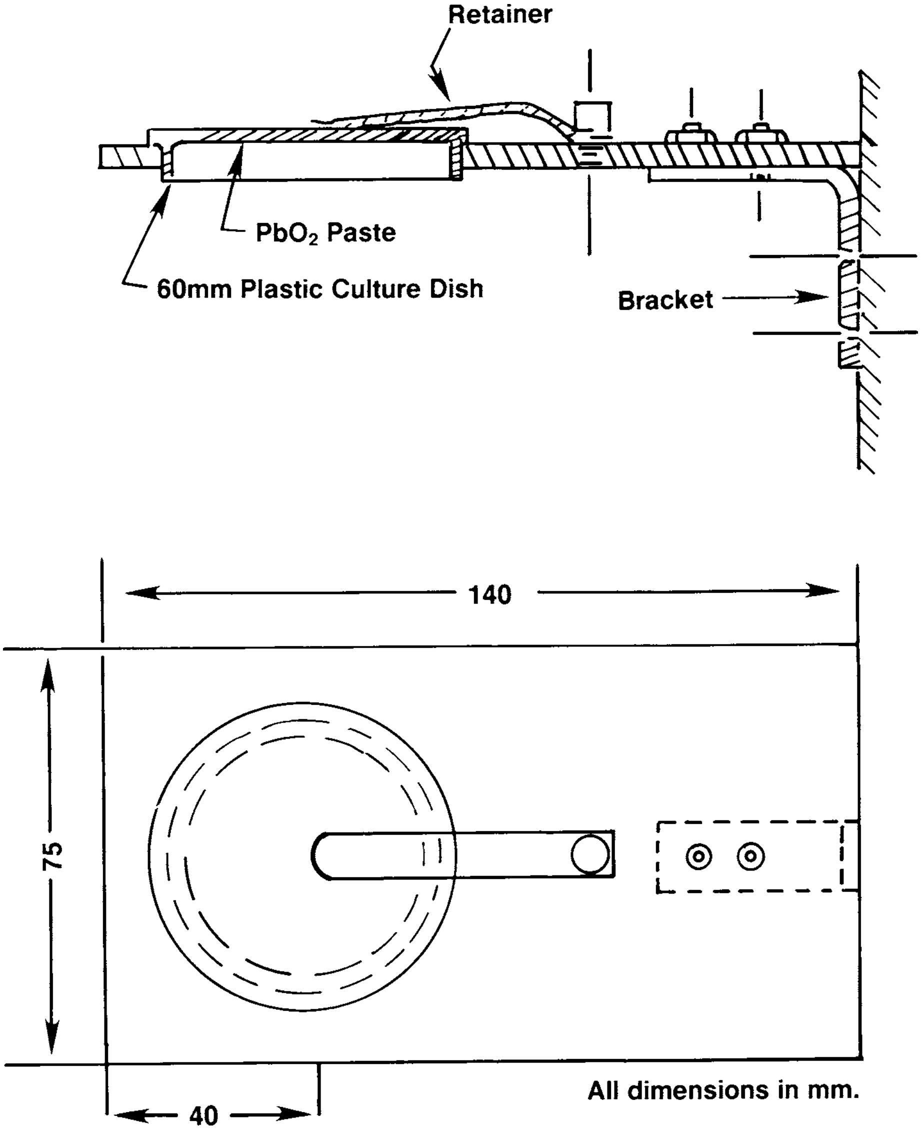
[4] Huey, N. A., "The Lead Dioxide Estimation of Sulfur Dioxide Pollution," *Journal of the Air Pollution Control Association*, Vol 18, No. 9, 1968, pp. 610–611.



All dimensions in mm.

FIG. 1 Sulfation Plate Holder

the device shall be removed from the bracket or holder and covered tightly to prevent additional sulfation. Analysis of the specimens shall be completed within 60 days of the completion of the exposure. The specimen identification, exposure location, and exposure initiation date should be recorded when the plate exposure is initiated. At the termination of exposure, the completion date should be added to the exposure records.

NOTE 3—The 30-day exposure is not very discriminating in areas of low SO_2 concentrations. Experience has shown that 60- to 90-day exposure may be necessary to develop a measurable SO_2 capture on the plate.

8.5 The specimen shall be analyzed for sulfate content using any established quantitative analysis technique.

NOTE 4—In conducting the sulfate analysis, it is necessary to remove the contents of the sulfation plate and solubilize the sulfate, for example, using a solution of sodium carbonate. It has been found that 20 mL of 50 g/L Na_2CO_3 (ACS reagent grade) is sufficient to solubilize the sulfate in this test method in a 3-h period. Thereafter, conventional sulfate analysis can be employed, for example, by barium precipitation and either gravimetric or turbidimetric analysis (see Test Method D516).

9. Calculation

9.1 The sulfate analysis provides the quantity of sulfate on each specimen analyzed. This should be converted to an SO_2 capture rate, R, by the following equation:

$$R = (m - m_0) \times MWSO_2/(MWSO_4 \times A \times T) \qquad (1)$$

where:

m = mass of sulfate found in the plate, mg,
m_0 = mass of sulfate found in a blank (unexposed) plate, mg,
$MWSO_2$ = 64,
$MWSO_4$ = 96,
A = area of the plate, m^2, and

T = exposure time of the plate, days.
R = SO_2 capture rate, mg SO_2/m^2 day.

9.2 The SO_2 capture rate may be converted to equivalent SO_3 or SO_4 values if desired, but for comparison purposes, SO_2 rates shall be used.

9.3 The average value and standard deviation of the values should be calculated according to Guide G16.

NOTE 5—The maximum sulfur dioxide capture rate for sulfation plates is 9000 mg/m^2 day, and for cylinders it is 5000 mg/m^2 day.

10. Report

10.1 The report shall include the following information:

10.1.1 A description of the exposure site and the locations where the plates or cylinders were exposed, including the bracket identity number or designation and the location on the exposure stand,

10.1.2 The exposure initiation and termination dates of plates or cylinders,

10.1.3 The identification numbers and sources of the sulfation plates or cylinders if they were obtained from a commercial source,

10.1.4 The calculated SO_2 capture rates for each specimen and the average and standard deviations for each site and exposure interval,

10.1.5 The sulfate analysis method, and

10.1.6 Any deviations from this practice.

10.2 Comparison should be made to previously determined values in ongoing monitoring programs.

11. Precision and Bias

11.1 Repeatability for a group of plates prepared in one batch and exposed for 30 days under essentially identical conditions, the standard deviation[5] has been found to be related to the average sulfation level by the equation given below:

$$\sigma_p = 0.079\, m_p \tag{2}$$

$$r_p = 0.22\, m_p \tag{3}$$

where:

σ_p = standard deviation of the plate SO_2 capture in mg SO_2/m^2 day,
m_p = average net SO_2 capture in mg SO_2/m^2 day,
r_p = repeatability of SO_2 capture in mg SO_2/m^2 day.

11.1.1 This relationship was determined in 10 runs with 6 or more plates per run. The standard error of estimate of the regression equation was 0.69 based on 8 degrees of freedom. This error is therefore the lower limit for σ_p, that is, the value of σ_p becomes a constant value of 0.69 mg SO_2/m^2 day when $\bar{m}$ is less than 8.8 mg SO_2/m^2 day and the repeatability is a constant 1.93 mg SO_2/m^2day.

11.2 The repeatability of lead peroxide cylinders was estimated from results of a study in which forty consecutive measurements were taken at two sites in Japan using both the lead peroxide cylinder and the sulfation plate technique. The standard deviation of the slope of the correlation line divided by the slope was assumed to be a reasonable maximum value for the ratio of the coefficient of variation for the plates This is expressed by the relation shown in Eq 4.

$$\sigma_c = 0.0577\, m_c \tag{4}$$

$$r_c = 0.162\, m_c \tag{5}$$

where:

σ_c = standard deviation of the cylinder average in mg SO_2/m^2day
m_c = average net SO_2 capture measured by the cylinder devices in mg SO_2/m^2day,
r_c = repeatability of the SO_2 capture by the cylinder method in mg SO_2/m^2day.

However, the standard error of estimate of the regression equation derived from the results of this study was 0.0312 mg SO_2/m^2day, and therefore this is the lower limit for σ_c when the m_c value is below 0.54 mg SO_2/m^2day. The repeatability in this case is 0.0847 mg SO_2/m^2day.

11.3 *Reproducibility*—Reproducibility in the case of these measurements is not applicable, because the conditions at any site cannot be reproduced, they exist only for the time measured.

11.4 *Bias:*

11.4.1 *Sulfation Plate*—Although the dry deposition of SO_2 from the atmosphere is directly related to the gaseous SO_2 concentration in the ambient air, (see Fig. 2), the deposition rate is also controlled by other factors such as wind velocity, specimen size and orientation, and temperature. The lead peroxide sulfation plate is considered to be a reliable measure of SO_2 deposition within the limitation discussed in this section. Consequently, this procedure for measuring atmospheric SO_2 dry depositions is defined only in terms of this practice.

11.4.2 *Lead Peroxide Cylinder*—The comparative study at the Japanese sites, Chosi and Tokyo, showed that the SO_2 deposition rate as measured by the sulfation plates was 1.28 times greater than that of the cylinders. Calculation based on natural convection heat transfer coefficients for a horizontal surface versus a vertical cylinder showed a ratio of 1.18. Reynolds analogy states that the mass transfer ratios should be equivalent to the heat transfer ratios, indicating that the plate method should give values 1.18 times the cylinder method. However, it must be noted that the cylinder method employs a 3.5 factor greater specimen area than the plate method and that improves their sensitivity, especially at low SO_2 levels.

11.5 Other methods of measuring SO_2 dry deposition include a wet candle technique (Test Methods D2010/D2010M).

12. Keywords

12.1 atmospheric corrosion; exposures; lead peroxide cylinder; measurement; plate preparation; sulfate analysis; sulfation plates; sulfur dioxide

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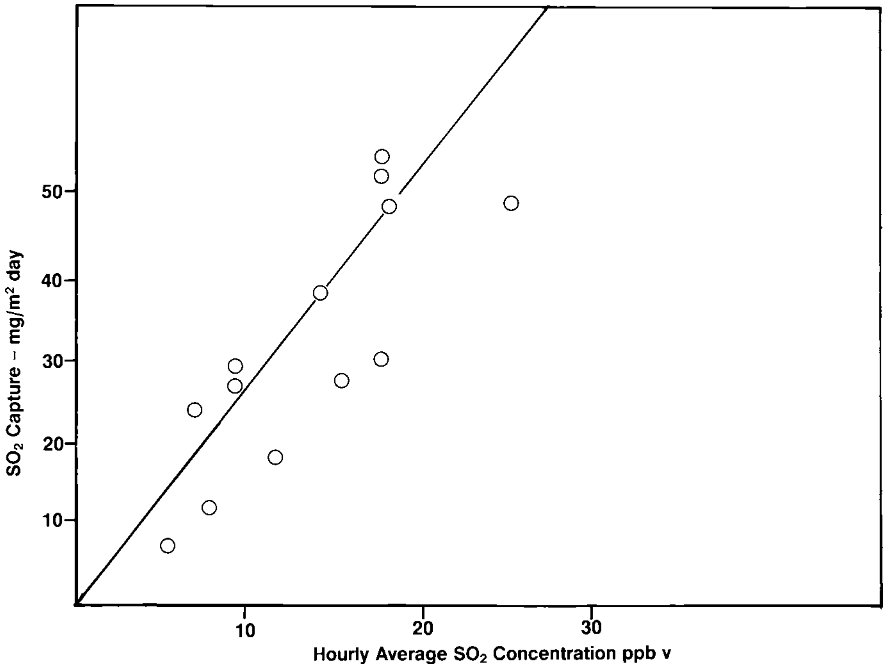
[5] Levadie, B., "Sampling and Analysis of Atmospheric Sulfur Dioxide with the Lead Dioxide Plate (Huey Plate)," *Journal of Testing and Evaluation*, Vol 7, No. 2, March 1979, pp. 61–67.



NOTE 1—A regression analysis on these results yielded the following least squares fit of the data.

$$R = (2.216 \pm 0.016)V$$

where:

R = the SO$_2$ capture rate in mg SO$_2$/m^2 day, and
V = the average hourly volumetric SO$_2$ concentration in parts per billion.

The correlation coefficient for this data set was 0.917 and the standard error of estimate was 7.5 with 13 df.

FIG. 2 Correlation Between Sulfation Plate Results and Mean Volumetric SO$_2$ Concentration

APPENDIXES

(Nonmandatory Information)

X1. SULFATION PLATE PREPARATION

INTRODUCTION

The following practice may be used to prepare sulfation plates:

X1.1 Bond filter paper circles to the bottom of polystyrene culture (petri) dishes. Either a 50-mm to 60-mm dish size is convenient. The bonding process is carried out by placing a filter paper circle, rough side up (S & S grade 30 is acceptable) in the bottom of the dish. Paper is bonded to the plate by adding reagent grade acetone from a wash bottle until the filter just becomes saturated. Avoid splashing acetone on the walls or outside the dish. Press the paper firmly with a glass rod so that all parts of the filter are pressed into the dish. Allow acetone to evaporate. One 900-mL batch of lead peroxide will cover about eighty 50-mm plates or fifty-five 60-mm plates. The bonding may be carried out well in advance of the plate preparation procedure.

X1.2 Place a batch of bonded plates, eighty 50-mm or fifty-five 60-mm plates, in a rack and rinse with Specification D1193 Type IV purified water. Then fill plates with water again and allow to stand for one hour. Pour water out and refill one-quarter to one-half with Specification D1193 Type IV purified water.

X1.3 Add 3.5 g of gum tragacanth and 900 mL Specification D1193 Type IV purified water to a high speed blender container. Set at low speed and blend for 2 h.

X1.4 Pour the contents of the blender into a 1 L beaker and return 350 mL of the solution to the blender container. Pulp 3.5 g of filter paper in the 350 mL of gum solution with the blender set at a moderate speed until the mixture appears smooth and uniform.

X1.5 Return 400 mL of the gum solution previously removed from the blender and blend at moderate speed for 1 min.

X1.6 Turn the blender to high speed and add 112 g of lead peroxide. Blend for 2 min and turn the blender back to low speed.

X1.7 Carefully pipet 10 mL of the mixture into each 50-mm plate or 15 mL into each 60-mm plate. Make sure mixture spreads uniformly through the water layer in the plate to the edge of each plate.

X1.8 Place the rack of plates in an oven set at 40 to 50°C for 20 h.

X1.9 Remove plate from oven and allow to cool. Seal plates with tight fitting covers to preserve until the exposure begins.

X1.10 Plates shall be numbered and placed on exposure within 120 days of preparation. Commercially obtained plates may be retained for up to one year before exposure. Retain at least one plate from each batch as a blank.

X2. LEAD PEROXIDE CYLINDER PREPARATION

INTRODUCTION

The following practice is based on ISO 9225:

X2.1 Cylinder

X2.1.1 Traditionally, a 31.8 mm diameter ceramic cylinder 150 mm long has been used as the form to hold the fabric collecting surface. However, a 1 in. plastic pipe with an outer diameter of 33.4 mm and 150 mm in length may also be used. In the case of a plastic pipe, the diameter may be machined to 31.8 mm, or the fabric cover increased to 105 mm in length. Plastic pipe materials such as Type 1 PVC (unplasticized), polypropylene, PTFE, polycarbonate, HDPE, or acrylic polymer would all be suitable. If a plastic pipe is used the top should be plugged and a threaded connection may be used on the bottom to secure it to the stand. The surface of the pipe may also be roughened if necessary to improve the adhesion to the fabric cover.

X2.2 Cut a 100 mm long piece of broad cloth with a thread count of 60 and a width of 100 mm, and attach it to cylinder centering it along the 150 mm length. Nylon strip ties may be used to hold the cloth to the cylinder.

X2.3 Dissolve 2 g of tragacanth gum powder in 10 mL ethanol, and add it to 190 mL of Specification D1193 Type IV purified water while stirring vigorously.

X2.4 Add 5 mL of the gum tragacanth solution to 5 g of lead peroxide powder, ASC reagent grade PbO_2, with a particle size of less than 149 µm and no measurable sulfate. Mix the liquid with the powder thoroughly to form a paste.

X2.5 Coat the cloth on the cylinder with the lead peroxide paste uniformly over the cloth area to form a uniform coating. Allow the coated cylinder to air dry and place it in a sealable container. It should be kept in this container until it is exposed.