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AN INDICATOR FOR THE DETECTION OF SULPHUR DIOXIDE FROM CELLS AN--ETC(U)
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Air Force Aero Propulsion Laboratory

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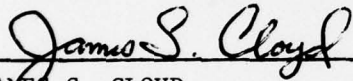
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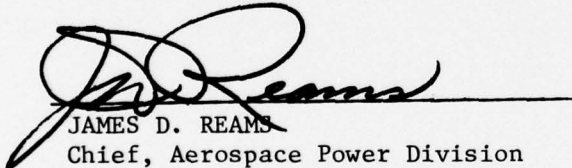


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents the results of the experimentation for the development of a chemical indicator for use in the detection of sulfur dioxide. This indicator has application for use with lithium-sulfur dioxide cells/batteries and with cells and batteries in which thionyl chloride or sulfuryl chloride is used as the active cathode. A depletion or sulfur dioxide from a lithium-sulfur dioxide cell of battery with subsequent use may produce unsafe conditions for the user. Both thionyl and sulfuryl chloride undergo hydrolysis in (cont'd)		

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ambient humidity and produce amounts of sulfur dioxide. This indicator can be used as a warning device for leakage or venting in these types of cells and batteries and consists of potassium chromate adsorbed onto a silicon powder with subsequent suspension in a silicon rubber material.

FOREWORD

This report contains the results of an effort to develop an indicator system for the irreversible detection of Sulfur Dioxide from defective cells or batteries using Sulfur Dioxide as the active cathode material. The work was performed in AFAPL/POE-1 of the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3145 and Task 314522. The effort was conducted by James S. Cloyd/AFAPL/POE-1 during the period 15 March 1978 to 15 May 1978.

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TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	EXPERIMENTAL	3
III	SUMMARY OF RESULTS	6
IV	DATA	7
V	CONCLUSIONS	13

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Test Apparatus for SO ₂ Exposure	4
2	Indicator Material and Indicator with Adhesive	7
3	Indicator After SO ₂ Exposure	8
4	Comparison of Indicator Before and After SO ₂ Exposure	10
5	Exposed Indicator Material After Storage	11
6	A Comparison of Unexposed, SO ₂ Exposed, and SO ₂ Exposed Indicator Samples with Storage	12

LIST OF TABLES

TABLE		PAGE
1	Chemical Indicator Systems	4
2	Adhesives for Indicator Incorporation	5
3	SO ₂ Exposure Test	9
4	SO ₂ Exposure Test on Indicator with Adhesive	9

SECTION I
INTRODUCTION

With Air Force requirements for higher energy power systems, the development of safe, reliable, high energy electrochemical power sources is imperative. One such high energy couple, currently under a Manufacturing Technology Program, is the lithium-sulfur dioxide system. Lithium (Li), a highly reactive solid, is used as the anode, while sulfur dioxide (SO_2), a caustic gas, acts as a depolarizer/active cathode. This electrochemical system has been proven to have the capability to supply relatively high current densities at extreme environmental conditions, a requirement for numerous Air Force applications. However, loss of SO_2 from Li- SO_2 cells and batteries has been found to produce conditions which may be hazardous to the user.

Under conditions of cell reversal with a deficiency of SO_2 , incidents of explosion and/or venting with fire have been observed. The causes of these events is not fully understood. One approach under consideration to help reduce the potential for these occurrences is the use of a lithium-limited composition. In the event, however, that SO_2 is lost by leakage around weldpoints or a defective hermetic seal or by venting, the limited composition no longer exists and hazardous conditions may arise. As a result, detection of SO_2 loss from a Li- SO_2 cell or battery is necessary.

Also under development are high energy density electrochemical systems using the lithium anode and thionyl chloride or sulfuryl chloride as the depolarizer/active cathode. It is known that thionyl chloride and sulfuryl chloride each react with water to form sulfur dioxide and sulfurous acid. If leakage or venting of either thionyl chloride or sulfuryl chloride occurred from a cell or battery, sulfur dioxide will be

produced from reaction with atmospheric humidity. Detection of a depletion of either thionyl chloride or sulfuryl chloride from cells or batteries of these types is therefore possible with an indicator for exposure to SO_2 .

It is known that certain chemical agents such as potassium permanganate, potassium dichromate and potassium chromate change color when exposed to SO_2 . G.D. Patterson and M.G. Mellon developed a process for SO_2 detection by impregnating silica gel with ammonium vanadate, potassium iodate or potassium periodate (reference 1). This method required an aqueous medium. It was the objective of this work to develop a chemical system which would change color upon SO_2 exposure in an air dry environment. This system could then be incorporated with Li- SO_2 cells and batteries as a warning device to the user that SO_2 has been lost and the use of that cell or battery may produce hazardous conditions.

The chemical indicator for detection of SO_2 from cells and batteries require these characteristics as an effective warning device for SO_2 :

1. React instantly with low levels of SO_2
2. Require little or no water for the reaction to occur
3. Provide a distinct color change upon SO_2 exposure
4. React irreversibly

After determination of the appropriate indicator according to the criteria listed above, it was necessary to develop a method of incorporating the indicator with the cells or batteries for proper detection of SO_2 . Proper attachment of the indicator to the cell or battery would require that the system be able to demonstrate:

1. The ability to attach the active indicator material to the surface of the cell or battery
2. Inertness to indicator reaction
3. The ability to allow visible detection of indicator color change

SECTION II

EXPERIMENTAL

A description of the chemicals tested, substrate materials used, and treatment conditions is given in Table 1. The test apparatus used for determining reactivity to sulfur dioxide is pictured in Figure 1. The apparatus was designed for visual inspection during the test and all used SO_2 was passed through a dilute solution of potassium hydroxide to prevent atmospheric contamination. All tests were performed in a vented laboratory hood. All indicator components ($\sim 0.5\text{g}$) were dissolved in 250 ml of distilled water. The indicator in solution was then adsorbed onto an inert substrate material such as Chromosorb W from Fisher Scientific Company and Cabosil manufactured by Cabot, Inc. The substrate material (~ 20.0 grams) was added to the indicator solution and stirred for several hours. The slurry was then spread into sheets and air dried. The material was then tested for sulfur dioxide reactivity.

After determination of the appropriate chemical indicator and substrate material, several commercially available adhesives were tested for possible use as a means of incorporating or attaching the chemical indicator to the cells or batteries containing SO_2 . Different ways of using the adhesive to hold the indicator were tested. In some samples, the indicator was applied to the surface of the adhesive, while in others blending of the indicator material with the adhesive until an even dispersion of indicator in adhesive was tested. A description of adhesives tested, indicator treatment, and any initial effects of adhesive on the indicator material before SO_2 exposure is given in Table 2.

Reference 1: Patterson, G.D., and M.G. Mellon, Anal. Chem., 24, 1586, (1952).

TABLE 1
CHEMICAL INDICATOR SYSTEMS

SAMPLE NR	Indicator Chemical Tested	Substrate	Initial Color	Treatment
1	Potassium Permanganate	Chromosorb W	Purple	air dry overnight
2	Potassium Dichromate	Chromosorb W	Yellow	air dry, 3 days
3	Potassium Dichromate	Chromosorb W	Yellow	air dried, 3 days one drop H ₂ O added
4	Potassium Dichromate	Cabosil	Yellow	air dried, 2 days no H ₂ O added

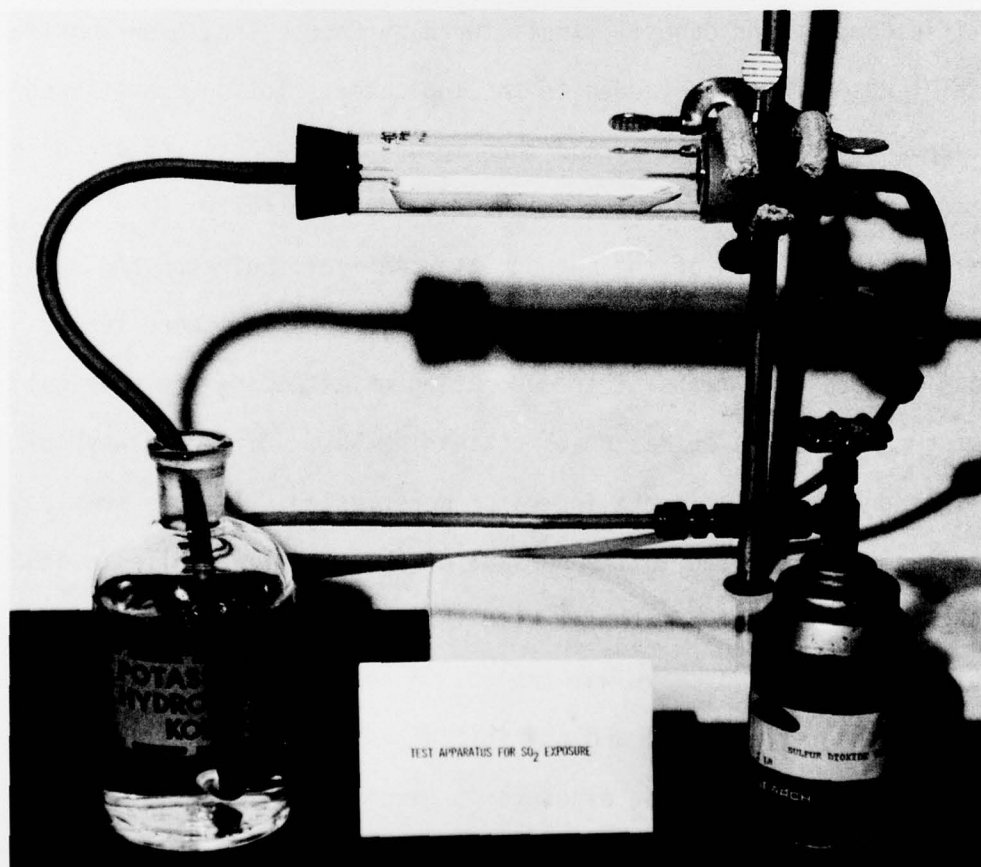


Figure 1. Test Apparatus for SO₂ Exposure

TABLE 2

ADHESIVES FOR INDICATOR INCORPORATION

Adhesive	Treatment	Effect of Adhesive on Indicator
Elmer's Glue	indicator placed on surface of adhesive	slight indicator reaction w/contact to adhesive
Elmer's Glue	indicator mixed w/adhesive	indicator change caused by adhesive
RTV Silicon Rubber	indicator placed on surface of adhesive	no effect
RTV Silicon Rubber	indicator mixed w/adhesive	no effect
plexiglass/methylene chloride	indicator placed on surface of adhesive	no effect
plexiglas/methylene chloride	indicator mixed w/adhesive	no effect

SECTION III
SUMMARY OF RESULTS

The development of a chemical indicator/warning device for the detection of SO_2 loss from a Li-SO_2 cell or battery is summarized.

1. A low concentration of potassium dichromate was adsorbed onto Chromosorb W, a product of the Fisher Scientific Company, and was dried and tested for reaction with SO_2 . It was found that this substance required a higher water content than could be obtained with ambient humidity in order for a color change to occur.

2. Cabosil, a silicon powder from the Cabot Corporation, has greater hygroscopic character than Chromosorb and, therefore, has a greater potential as an appropriate inert substrate for this reaction. A low concentration of potassium dichromate was adsorbed onto Cabosil and the resultant mixture was air dried. This substance was found to undergo a color change upon exposure to SO_2 without additional moisture.

3. Two adhesives were found suitable as a means of incorporating the Cabosil/indicator mixture to Li-SO_2 cells or batteries. One adhesive was prepared by dissolving plexiglass shavings in small amounts of methylene chloride to form a paste. This material did not react with the potassium dichromate, but upon SO_2 exposure, only the surface exposed regions of Cabosil changed color. It was determined that RTV Silicon Rubber, a white silicon sealer, was the most compatible adhesive. The reactive Cabosil mixture could either be spread on the surface of the RTV Silicon Rubber or the mixture could be dispersed through a sample of RTV Silicon Rubber with similar results. In both cases a distinct color change from yellow to blue-green was observed upon exposure to SO_2 .

SECTION IV

DATA

In an attempt to determine the most effective indicator compound and substrate material, several combinations were tested by exposure to SO_2 . The observations made during these tests are presented in Table 3.

It can be seen from Table 3 that potassium dichromate adsorbed onto Cabosil, a tradename for finely powdered silicon dioxide from Cabot, Inc., proved to be the most effective composition for SO_2 detection. Indicator reaction occurred at room ambient conditions without additional water. A sample of this mixture is pictured in Figure 2 (left) to show indicator color before exposure to SO_2 .

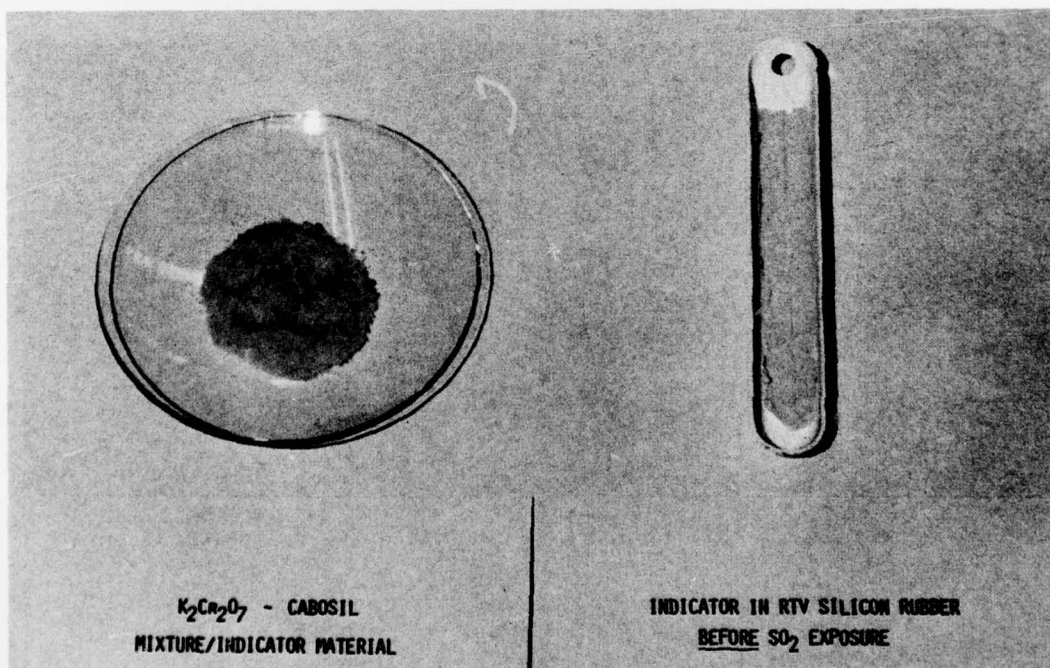


Figure 2. $\text{K}_2\text{Cr}_2\text{O}_7$ - Cabosil Indicator Material (left), Indicator Mixed with Adhesive (right).

Adhesives were tested in two configurations. One sample contained indicator material dispersed on the surface of the adhesive. Another sample contained indicator material mixed thoroughly with the adhesive. Effects of adhesive material on indicator behavior were noted before and after exposure to SO_2 . The plexiglass-methylene chloride mixture produced a clear, viscous substance which, upon evaporation of methylene chloride, formed a hard material similar to plexiglass.

Results shown in Table 4 indicate that the RTV Silicon Rubber most closely fits the desired characteristics listed previously. A sample of this indicator mixed with RTV Silicon Rubber and then exposed to SO_2 is shown in Figure 3. RTV Silicon Rubber made by General Electric is a white adhesive which can allow for visible detection of the indicator color change from yellow to blue-green. Mixture of indicator with RTV

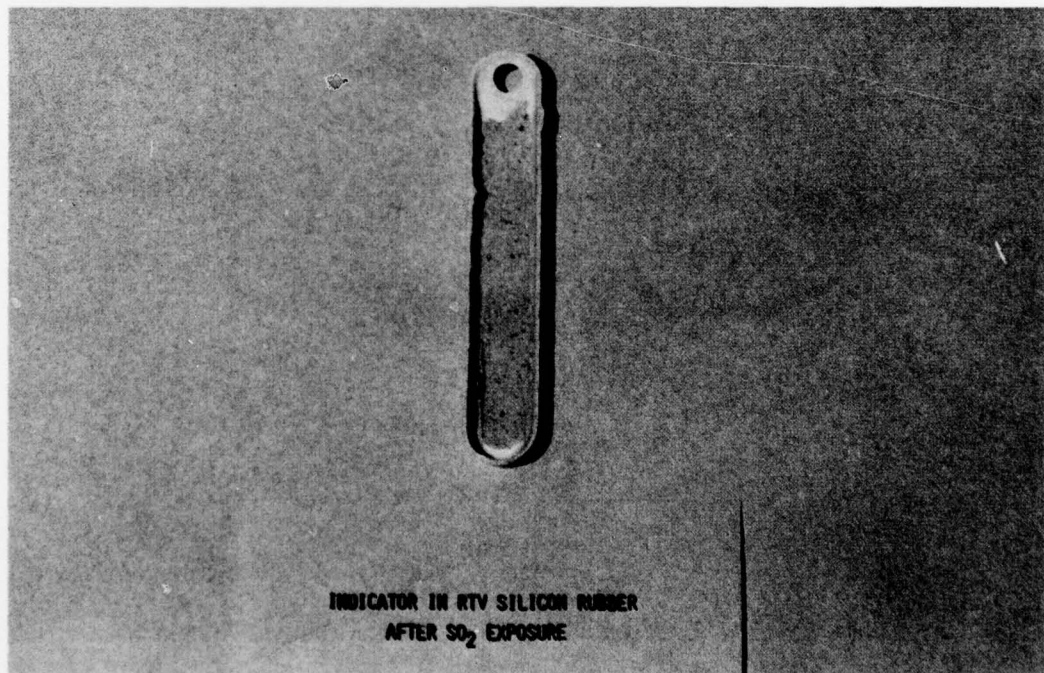


Figure 3. Indicator in RTV Silicon Rubber After SO_2 Exposure

TABLE 3
SO₂ EXPOSURE TEST

Sample	Indicator Compound	Substrate	Initial Color	SO ₂ Exposure Test Result/ Final Color
1	Potassium Permanganate	Chromosorb	purple	no test performed light sensitive/brown
2	Potassium Dichromate	Chromosorb	yellow	no color change with SO ₂
3	Potassium Dichromate	Chromosorb	yellow	immediate reaction/bl-grn
4	Potassium Dichromate	Cabosil	yellow	immediate reaction

TABLE 4
SO₂ EXPOSURE TEST ON INDICATOR WITH ADHESIVE

Adhesive	Treatment	SO ₂ Exposure
Elmer's Glue	indicator placed on surface of adhesive	slight indicator change w/SO ₂
Elmer's Glue	indicator mixed w/ adhesive	indicator change without SO ₂
RTV Silicon Rubber	indicator placed on surface of adhesive	indicator change at surface of adhesive
RTV Silicon Rubber	indicator w/adhesive	indicator change throughout adhesive mixture
plexiglass/ methylene chloride	indicator placed on surface of adhesive	indicator change at surface of adhesive
plexiglass/ methylene chloride	indicator mixed w/ adhesive	indicator change at surface of adhesive

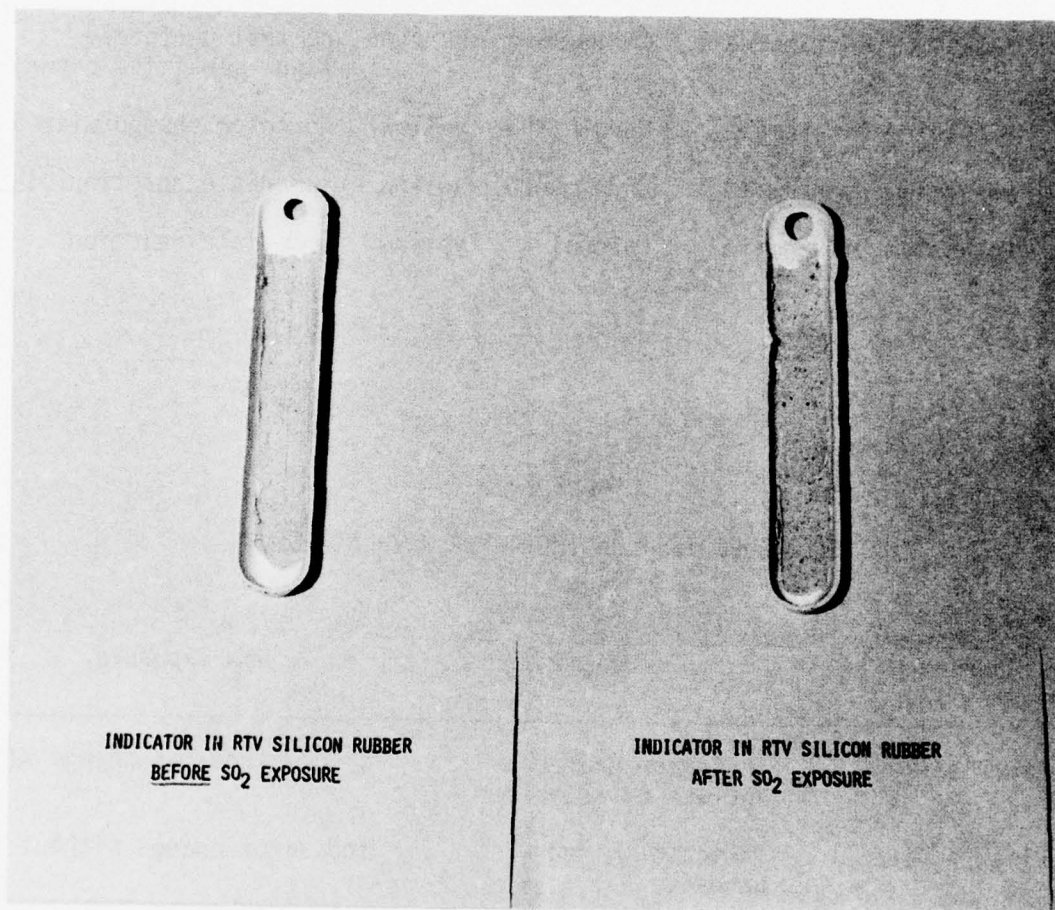


Figure 4. Color Comparison Between Unexposed and Exposed Indicator Material to SO₂

Silicon Rubber produced a yellow adhesive which did not affect indicator sensitivity to SO_2 . Figure 4 shows a color comparison between the yellow, unexposed indicator material and the blue-green, SO_2 exposed indicator material. It was noted that the composition of this indicator-adhesive mixture had a porous structure when compared to pure RTV Silicon Rubber, a relatively non-porous material. Porous structure was realized by observation of indicator change with SO_2 throughout the thickness of the test sample.

Irreversible indicator reaction of SO_2 is a necessary characteristic for proper recognition of SO_2 loss from a cell or battery. A sample of indicator material was therefore exposed to SO_2 and was stored at room ambient conditions for several weeks. It can be seen from Figure 5 that the indicator material exposed to SO_2 shows no reversible character after room temperature storage. The indicator is therefore irreversible under normal conditions. For comparison, unexposed, exposed, and exposed samples with storage are presented together in Figure 6.

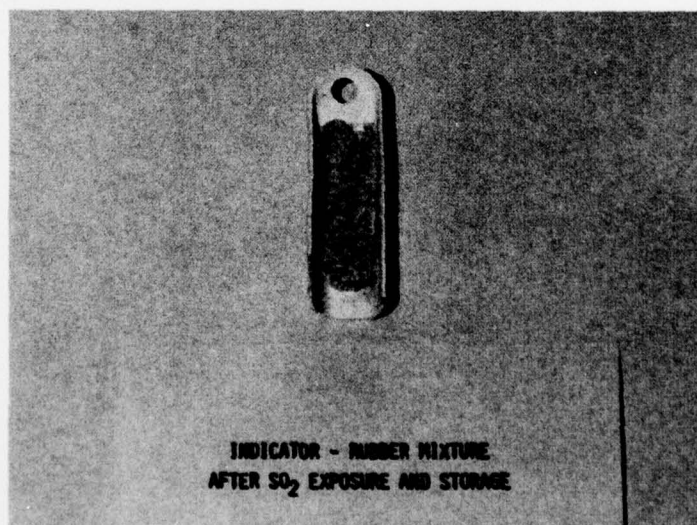


Figure 5. SO_2 Exposed Indicator Material After Storage

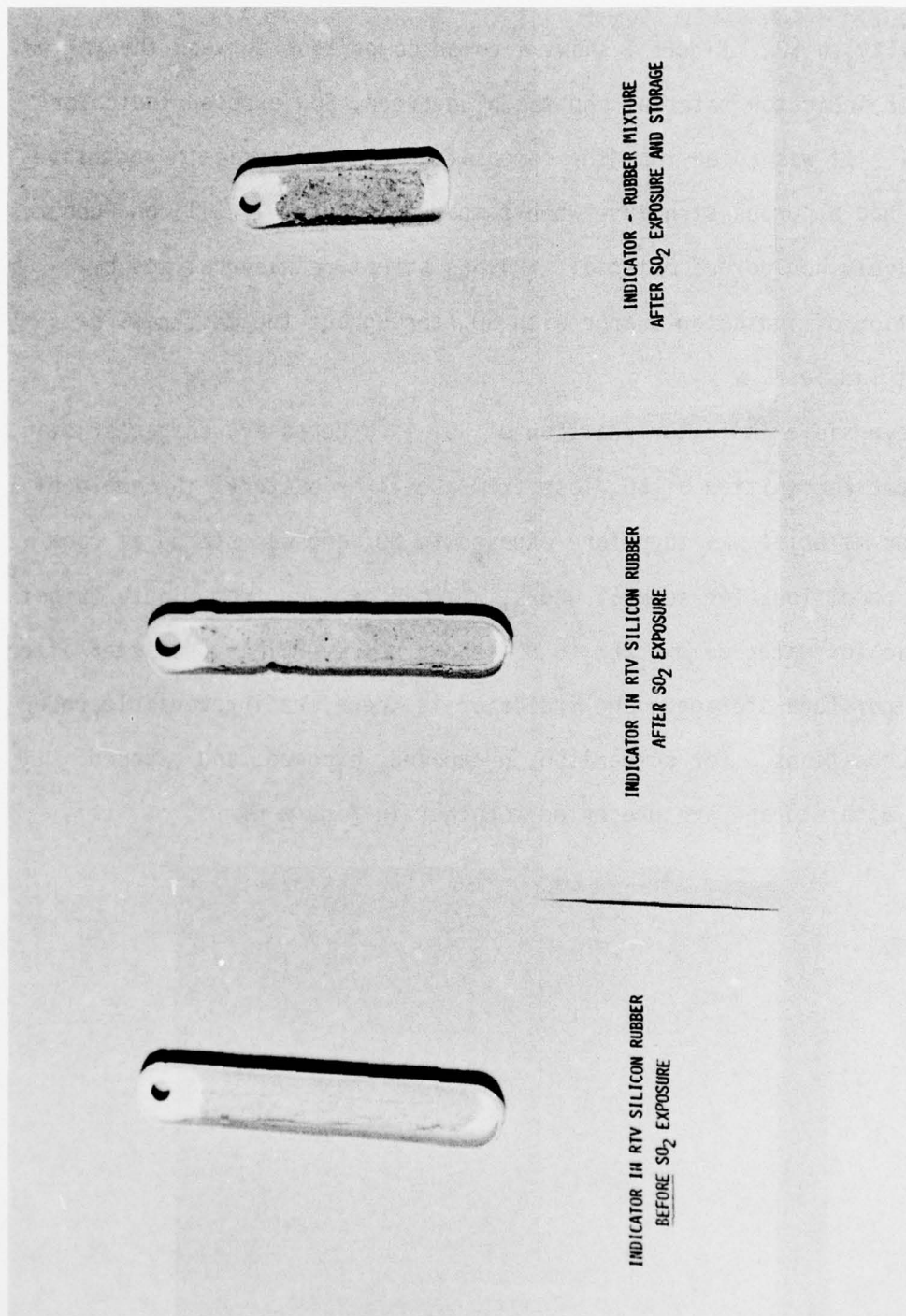


Figure 6. A Comparison of Unexposed, SO₂ Exposed, and SO₂ Exposed Indicator Samples with Storage

SECTION V
CONCLUSIONS

The major conclusion of this work is that an indicator/warning device has been developed which, upon exposure to SO_2 from lithium-sulfur dioxide, thionyl or sulfuryl chloride cells or batteries will warn the user of a defective, potentially hazardous cell or battery. This indicator, potassium dichromate adsorbed onto Cabosil, can be incorporated on the cell or battery casing and around the venting mechanism by attachment with RTV silicon rubber. This yellow material will react with SO_2 that has escaped from the cell or battery and will turn a dull blue-green color as an indication of a potential hazard.