Patented Sept. 11, 1951 2,567,251

UNITED STATES PATENT OFFICE

2,567,251

ANALYTICAL SELENIUM STRIP AND METHOD OF PREPARATION THEREOF

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No Drawing. Application July 12, 1949, Serial No. 104,390

8 Claims. (Cl. 23—232)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented in any country, may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to me of any royalty thereon.

This invention relates to a novel selenium strip useful for analytical purposes and to methods for its production.

It is known in the art that mercury vapor in air or other gases can be detected or its proportion determined by contact of the mercury-containing gas with selenium sulphide strip. In this technique, the selenium sulphide strip is exposed to the atmosphere containing mercury whereby the paper becomes blackened due to formation of mercury sulphide, mercury selenide, or both. Thus the quantity of mercury can be determined by comparison of the degree of blackening with standard pre-blackened strips or by measuring the length of the darkened area along the strip and comparing with standards.

The known selenium sulphide strips suffer from several disadvantages. Thus one type of strip is prepared by rubbing powdered selenium sulphide on a strip of paper or by painting the strip of paper with a dispersion of selenium sulphide. In strip so prepared the amount of active material is not uniform on all areas of the strip. Uniformity is, of course, particularly important when the concentration of mercury is to be determined by measurement of the length of the blackened area. The non-uniformity is caused by the fact that in the known methods of preparing the strip, solid selenium sulphide either powdered or in a suspension is applied to the paper and it is virtually impossible to spread this solid material uniformly over the entire surface of the strip. The second disadvantage is that the known selenium sulphide strips are temperature sensitive. The length of blackening obtained with a standard mixture of mercury vapor and inert gas will vary depending on the temperature at which the strip is maintained. As a result, the temperature of the gas being analyzed must be carefully controlled to obtain accurate results.

Another known strip is made by soaking paper

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in selenious acid solution and then exposing the treated paper to an atmosphere of hydrogen sulphide. The paper is dried, then baked in an oven at 140° C. This baking step is a critical part of the process as it increases the stability of the selenium sulphide strip. In this process it is virtually impossible to prepare paper of reproducible characteristics. This is so because in the baking step the temperature and time of baking have a critical effect on sensitivity. Since the baking process cannot be carried out in exactly the same way each time, each batch of selenium sulphide strip must be separately calibrated. Further, this strip is also temperature sensitive. That is, the length of blackening obtained with a standard mixture of mercury vapor and inert gas will vary depending on the temperature at which the strip is maintained.

I have found that the presence of sulphur is actually unnecessary and I use selenium as the sole active agent. The selenium strip according to my invention is free from the disadvantages of the selenium sulphide strips referred to above. The selenium is uniformly deposited throughout the strip thus accurate results are possible. This uniformity is obtained because the selenium is applied to the paper in the form of a solution. The importance of this is that in a solution the concentration of selenium is uniform throughout and the particles (ions) in solution are all of the same size. When backing strip is immersed in a solution, the strip will thus be uniformly impregnated with selenium. Such result is not possible when working with non-uniform materials such as suspensions or dry powders. In such case mechanical manipulations such as stirring in the case of a suspension or careful spreading in the case of a dry powder are required in an attempt to obtain uniform coverage. However, even with such manipulation uniform coverage is not possible because of varying particle size and/or concentration of the material.

It has also been observed that selenium strip produced in accordance with this invention is not temperature-sensitive. For example, the temperature may be varied from 120° to 200° C. and the length of blackening produced by a standard sample of mercury-inert gas mixture will be substantially the same.

Further, the selenium strip according to this

invention can be prepared with reproducible characteristics. That is, if the concentration of the seleno-cyanate solution is kept constant and the paper is of uniform character then each batch of selenium strip will be identical in its sensitivity. Thus if one batch of strip is calibrated the data obtained will be applicable to all batches prepared from the same type of paper and at the same concentration of selenocyanate.

It is to be noted that the selenium strip produced in accordance with this invention contains the selenium in an active state. By this is meant that if the strip is exposed to mercury vapor, the mercury will react with the selenium to form mercury selenide. Selenium does not always exist in this active state. For example, ordinary powdered selenium available in commerce is virtually unreactive with mercury vapor.

Further, the selenium strip of this invention is stable. Samples thereof have been stored for 6 months and upon testing them, it has been found that their response is identical with the strip as freshly prepared.

Another significant property of the selenium strip of this invention is that when it is contacted with mercury vapor, the degree or length of the blackening obtained is substantially directly proportional to the concentration of mercury. This is an important attribute as it permits accurate determination of the unknown mercury concentration by extrapolating from a few standard determinations. The fact of this linear relationship is shown in Tables I and II below.

The novel selenium strip of this invention is prepared in the following manner:

(1) A backing material is first selected. I prefer to use a purified chemical filter paper but one may also use other forms of uncoated paper, cloth, asbestos fiber, or other porous sheet material. The backing material is then soaked in a solution containing selenocyanate ions, then drained to remove excess liquid. I prefer to use for the impregnation an aqueous solution of potassium selenocyanate, although any water-soluble selenocyanate is suitable, for example, sodium selenocyanate, ammonium selenocyanate, etc. The point is, of course, that the solution contain selenocyanate ions, the particular cation being unimportant as long as the salt is soluble enough to give the desired concentration. The concentration used depends on the sensitivity desired for the finished strip—the lower the concentration of selenium, the higher will be the sensitivity. The length of blackening per unit amount of mercury is inversely proportional to the concentration of selenocyanate used in making the paper. Thus if a standard sample of mercury vapor-air mixture gives 20 mm. of blackening on strip which has been made with 0.01 molar selenocyanate solution then 10 mm. of blackening will be obtained with the same gas sample if the strip is made with 0.02 molar selenocyanate solution. Generally, the concentration of selenocyanate solution is correlated with the approximate range of mercury concentration to be measured. For very low mercury concentrations, the selenocyanate concentration may be as low as 0.005 molar while for high concentrations of mercury, the selenocyanate concentration may be as high as 1 molar. By proper correlation of selenocyanate concentration and expected mercury concentration, the length of blackening will then be of convenient length, for example, 2 to 5 inches, along a six-inch strip.

(2) The strip is then suspended, while wet, in an atmosphere containing acid vapors. For example the strip may be placed in a bell jar containing a beaker of hydrochloric acid. The particular acid is not important as long as it is volatile. Thus the vapors of nitric acid, hydrobromic, acetic or other volatile acids may be used. The result of this treatment is that the selenocyanate is decomposed into elemental selenium. The following equation illustrates the reaction, assuming that potassium selenocyanate and hydrochloric acid are the reagents employed:

$$KSeCN+HCl\rightarrow KCl+HCN+Se$$

The potassium chloride remains in the strip along with the elemental selenium and does not affect the use or activity of the strip. This reaction occurs very rapidly and it is preferred to expose the strip to the acid atmosphere for only a short period, i. e., about 5 seconds to about 30 minutes. It has been observed that the treatment for substantially longer periods tends to decrease the reactivity of the strip. In this treatment it is also necessary to apply the acid treatment while the strip is wet. If the strip is allowed to dry, the elemental selenium will still be formed but in an unreactive form.

(3) The acid-treated strip is then dried. This drying is preferably carried out by simply exposing the strip to the atmosphere. If desired, one may subject the strip to a current of air which may be heated to not greater than about 100° C. to hasten the evaporation of water.

The following examples disclose particular techniques within the scope of this invention, but it is to be understood that these examples are given only by way of illustration and not limitation. The abbreviation "ppm." used herein means parts per million.

Example I

A piece of 8''x8'' chemical filter paper was immersed in aqueous 0.01 molar potassium selenocyanate solution for about 2 minutes. The paper was then removed from the solution and a clip attached to one corner. The paper was then hung up by the clip in a closed container and allowed to drain for about 15 minutes. The drained paper was then hung in a large jar which contained a pool of concentrated hydrochloric acid at the bottom thereof and into which pool anhydrous hydrogen chloride had been bubbled for several minutes through a tube terminating in the pool of acid. The paper was subjected to the acidic atmosphere thus created for 15 to 30 seconds, the introduction of hydrogen chloride being continued during this period, then removed and hung in the air until dry. One inch margins on all four sides of the dry paper were then cut off and discarded. The remaining 6''x6'' sheet was cut into strips ⅛'' wide.

The selenium strips were then calibrated as follows: A strip was placed lengthwise in a glass tube having an inside diameter slightly larger than ⅛'' so that the strip fitted snugly in the tube. One end of the tube was open while a standard sample of air containing mercury vapor was introduced into the other end. During this process, the tube was positioned in a heating device to maintain the temperature at 125° C. The gas sample used had a volume of 40 ml. and was introduced at the rate of 15 ml./minute. After the strip had been subjected to the gas, it was removed from the tube and the length of the blackened area measured. This procedure was repeated several times employing each time a

different sample of air containing a known concentration of mercury vapor and the following results were obtained.

TABLE I

Concentration of Hg vapor	Length of blackening
P. P. M.	*Mm.*
14.5	6.2
41	16
68	29
93	41
113	51
134	60

These figures demonstrate that the length of blackening is substantially directly proportional to the concentration of mercury.

These calibration data are then used for a determination of an unknown gas sample. Thus if a strip of this paper is treated with an unknown gas sample under the same conditions as used in the calibration, the length of blackening is a measure of mercury concentration. For example, if the length of blackening obtained is 35 mm. then the mercury concentration is 78 ppm. For convenience one may plot on graph paper the concentration of mercury versus length of blackening and thus one can read directly on the graph the concentration of mercury corresponding to the length of blackening obtained.

Example II

Selenium strip was prepared exactly as described in Example I, the only difference being that in this case the concentration of potassium selenocyanate was 0.03 molar. The strip was calibrated as in Example I and the following results were obtained:

TABLE II

Concentration of Hg vapor	Length of blackening
P. P. M.	*Mm.*
70	10
123	17
194	28
264	38
335	49
375	54

These figures demonstrate that the length of blackening is substantially directly proportional to the concentration of mercury.

Example III

(Effect of temperature on selenium strip)

Selenium strip was prepared as described in Example I using a potassium selenocyanate concentration of 0.03 molar. A strip was placed lengthwise in a glass tube having an inside diameter slightly larger than ⅛'' so that the strip fitted snugly in the tube. One end of the tube was open while a standard sample of mercury-containing air was introduced into the other end. The tube was positioned in a heating device which could be regulated to obtain different temperatures. Since this experiment was intended to determine the effect of temperature on the strip, the tests were repeated at different strip temperatures while keeping the concentration of mercury constant. The volume of gas sample and rate of introduction were also kept

constant to give truly comparable results. The following results were obtained:

TABLE III

Temperature	Length of blackening
°*C.*	*Mm.*
103	31.0
124	31.1
142	31.1
164	30.5
187	32.1
203	31.5

The figures demonstrate that the selenium strip according to this invention exhibits a substantially uniform sensitivity over the temperature range set forth.

Control experiment A

(This experiment is not representative of this invention but is included to compare temperature sensitivity of the known strip with that of the invention.)

A prior art selenium sulphide strip such as that heretofore described was tested for effect of temperature exactly as set forth in Example III. The following results were obtained:

TABLE IV

Temperature	Length of blackening
°*C.*	*Mm.*
120	17.9
140	20.5
160	30.5
180	41.5
200	47.9
220	52.3

The selenium strip produced in accordance with this invention has a salmon color, thus on contact with mercury vapor the blackened (reacted) portion is easily distinguishable from the unreacted portion of the strip. The strip is adversely affected by light and thus should be stored in containers of metal or colored glass such as used for preservation of light-sensitive chemicals. The container should be closed to prevent darkening of the paper by contact with mercury vapor which may exist in the atmosphere of a chemical laboratory or other places where mercury is present. So stored the strip retains a constant sensitivity almost indefinitely.

Although I have stressed the particular use of the selenium strip for determination of mercury concentration by measuring the length of blackening, it is obvious that the use of the strip need not be so restricted. Thus the strip can be used for mercury determinations by comparison of the degree of blackening with standard samples or by other known colorimetric methods.

As stated heretofore, selenium strip of this invention is used for determination of mercury concentration in gases. One practical use for such technique is to carry out such determination on the atmosphere in laboratories or factories where mercury is being distilled—for example, in mercury refining plants or in a mercury vapor power plant. Another important use is where concentration of mercury vapor is to be determined in order to ascertain concentration of oxidizable gases in an atmosphere. For example, the concentration of hydrogen, carbon monoxide, ethylene, methane, ethane, formaldehyde, etc. in air or other gaseous atmosphere may be de-

termined by passing the gas in measured volume through a heated tube containing red mercuric oxide. A reaction occurs in which the oxidizable gas is completely oxidized and mercury is released in quantitative proportion to the concentration of oxidizable gas. Thus by measuring the concentration of mercury vapor issuing from the heated mercuric oxide one can compute the concentration of oxidizable gas. The oxidation reactions involved, in the case of ethylene and hydrogen, are illustrated by the following equations:

$$C_2H_4+6HgO \rightarrow 2CO_2+2H_2O+6Hg$$

$$H_2+HgO \rightarrow H_2O+Hg$$

Having thus described my invention, I claim:

1. The method of preparing a selenium strip which comprises impregnating a backing sheet with an aqueous solution of a water soluble selenocyanate, draining excess solution from the sheet, exposing the drained sheet to an acidic atmosphere, and drying the acid-treated sheet at a temperature not higher than about 100° C.

2. The method of preparing a selenium strip which comprises impregnating paper with an aqueous solution of a water soluble selenocyanate, draining excess solution from the paper, exposing the drained paper to an acidic atmosphere, and drying the acid-treated paper, at a temperature not higher than about 100° C.

3. The method of preparing a selenium strip which comprises impregnating paper with an aqueous solution of a water soluble selenocyanate, draining excess solution from the paper, exposing the drained paper to an acidic atmosphere for a period of time not longer than 30 minutes, and drying the acid-treated paper at a temperature not higher than about 100° C.

4. The method of preparing a selenium strip which comprises impregnating paper with an aqueous solution of potassium selenocyanate, draining excess solution from the paper, exposing the drained paper to an atmosphere containing hydrogen chloride, and drying the acid-treated paper at a temperature not higher than about 100° C.

5. The method of preparing a selenium strip which comprises impregnating paper with an aqueous solution of potassium selenocyanate, draining excess solution from the paper, exposing the drained paper to an atmosphere containing hydrogen chloride for a period of time not to exceed 30 minutes, and then drying it at a temperature not higher than about 100° C.

6. An analytical strip in which selenium is the sole active agent comprising sheet material uniformly impregnated with elemental red selenium, said strip exhibiting substantially equal sensitivity to mercury vapor in the range from about 120° C. to about 200° C.

7. An analytical strip in which selenium is the sole active agent comprising paper uniformly impregnated with elemental red selenium, said strip exhibiting substantially equal sensitivity to mercury vapor in the range from about 120° C. to about 200° C.

8. An analytical strip comprising paper uniformly impregnated with elemental red selenium, said selenium being the sole active component in the strip, said strip being stable, exhibiting substantially equal sensitivity to mercury vapor in the range from about 120° C. to about 200° C., and the degree of blackening of which when exposed to a gas containing mercury vapor is substantially directly proportional to the concentration of mercury vapor.

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