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CURRENT-RECTIFYING DEVICE.

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My invention relates to current rectifying and current modifying devices of the general nature of natural crystals, and more particularly relates to improvements in contact rectifiers, electric valves, photoelectric elements, contact detectors, and the like.

It has long been known that certain minerals such as galena and pyrite, as well as many others familiar to students of this subject, possess the characterstic of unilateral conductivity to a marked extent, these minerals permitting an electric current to pass much more readily in one direction than in another, under a given set of conditions. It is interesting to point out that this unilateral conductivity is not directly a chemical characteristic of the minerals however, since many mineralogically true specimens of both galena and pyrites do not show this characteristic of uni-lateral conductivity at all, while many other specimens show a high degree of uni-lateral conductivity or "sensitiveness" in certain spots, while other spots on the same mineralogical specimen show very much weaker uni-lateral conductivity, and frequently show no tendency toward uni-lateral conductivity at all, the electrical conductivity being exactly the same in either direction.

In a manner quite analogous to the unilateral conductivity of the minerals galena and pyrite, certain other minerals such as molybdenite and argentite show modified electrical conductivity in the presence of light, the minerals named, as well as many others known to those who have specialized in this subject, showing a very great difference in electrical conductivity, according to the degree which the specimen is irradiated with actinic or equivalent rays. It is interesting to point out that the analogy between the modified electrical conductivity of minerals such as molybdenite and argentite to actinic rays, and the uni-lateral conductivity of minerals such as galena and pyrites in the presence of alternating currents of high frequency, has a further remarkable extension in the fact that both photoelectric crystals and uni-laterally conducting crystals at times show negative or reverse characteristics, most specimens of molybdenite for example showing a lower electrical resistance in the presence of light, while some few specimens show increased resistance when illuminated, and most specimens of galena showing maximum conductivity in a direction from the specimen to a small point making loose contact with the crystal, although in very rare cases crystals of galena are found to show just the opposite conductivity.

The most careful study up to now has not furnished any full explanation of either uni-lateral conductivity or photoelectrical sensitivity, although these characteristics seem best capable of explanation by the theory that certain electrons in the molecular structural or crystal lattice are partly free to move, although not possessing the same degree of freedom that exists in metals or other materials of high electrical conductivity.

I have discovered simple and definite means by which I am able to controllably modify the electrically conducting characteristics of synthetic chemical compounds similar to those materials which show unilateral conductivity and photoelectric sensitivity in the natural minerals, and I can not only produce the same degree of unilateral conductivity and photoelectrical sensitivity which exists in natural minerals, but I am able by the practice of my present invention to obtain current modifying elements which possess a greater degree of rectifying ability, and which have a higher photoelectric sensitivity, than is possessed by natural minerals.

In order to more clearly explain the nature of the chemical and inter-molecular changes which I am able to bring about by the application of my present invention, I will make use of the assumption that solid bodies such as lead sulfide consists of atoms bound together by electrical forces in a structural lattice, and that in such bodies individual molecules do not exist. the entire mass of material being essentially a single molecule, as shown by the structure of the large number of such materials which have been determined by X-ray diffraction measurements. (W. L. Bragg, Proc. Camb. Phil. Soc. vol. 17, p. 43, (1912) and later papers.) I will further make use of the assumption that all atoms consist of a central positive charge, surrounded by one or more shells or layers

of electrons and that chemical reactions are the result of the sharing of electrons in the outer layers of the reacting atoms (G. N. Lewis, J. Am. Chem. Soc. vol. 38, p. 763, 1916, I. Langmuir, Jour. Am. Chem. Soc. vol. 38, p. 2221, 1916 and I. Langmuir, Jour. Am. Chem. Soc. vol. 41, p. 868, 1919). I will further make use of the assumption that the addition of an electron results in the reduction of the substance to which the electron is added, and the withdrawal of an electron results in the oxidation of the material from which such electron is withdrawn, it being of course remembered that the words oxidation and reduction are employed in a chemical sense, and wholly independent of whether or not oxygen is actually involved in the reaction (W. M. Clark, reprint No. 823 from Public Health Reports, 1923).

In making use of the assumptions stated above, I wish to particularly point out that my object is to enable the practical results which I obtain to be visualized to some extent, the whole question of sub-atomic phenomena and inter-atomic relationships being so complicated and difficult as to make some basic or fundamental concepts most helpful in clarifying the results which are obtained in practice from the treatment of a large number of seemingly very different materials. In making use of the above assumptions however, I wish to state that the practical results obtained are not and cannot in any way be affected by the truth or falsity of the concepts used in explaining them, although the work in regard to crystal and "mass" structure as determined by the X-ray diffraction method of Laue, Bragg and others, and the assumptions made by Lewis, Thompson and Langmuir in explaining the mechanism of chemical reactions, now appear to be well supported by a large amount of experimental evidence of a most convincing character.

In the practice of my invention I prefer to expose a body, such as sulfide of lead for example, to the simultaneous action of an electron-emitting reagent and an electron-absorbing reagent, existing together in equilibrium relationship, although I may expose the body to be treated separately and independently to each reagent, or alternately to the two reagents as alternative modifications of my process. As electron-emitting substances I prefer to use reducing materials such as hydrogen sulfide, sulfur or carbon bisulfide, and as an electron-absorbing reagent I prefer to use sulfur dioxide. Where the substance under treatment is exposed to the simultaneous action of both an electron-emitting and an electron-absorbing agent, it is desirable to avoid incompatible reagents, by which I mean reagents which undergo reaction at the temperature employed to such an extent as to materially displace the equilibrium relationship, or which permit free oxygen to be present in the reaction products of the mixture. As an example of a favorable pair of reacting materials I may mention carbon bisulfide as an electron-emitting substance, and sulfur dioxide as an electron-absorbing reagent, these two materials being capable of existing together at the temperatures employed in my process without material displacement of the normal equilibrium condition. As an example of an incompatible pair of reagents I may cite hydrogen sulfide and sulfur dioxide, these two materials tending to react at the temperature employed in my process to form sulfur and water vapor, the initial reacting materials being almost completely transformed into the reacting products named, and leaving an insufficient amount of the initial products to properly alter the electron lattice.

As my invention can be best understood by showing its actual application in the modifying of the electrically conducting characteristics of a chemical system of known properties, I will now describe in detail a method which I may employ in the preparation of a uni-laterally conducting material of high sensitivenes suitable for use as a detector of radio waves, starting from raw materials which possess substantially no electrical conductivity, and which do not possess the slightest tendency toward uni-lateral conductivity, and I will point out the steps by which these initially non-conducting and non-rectifying products may be transformed into a mass possessing a high degree of rectifying ability.

Preparation of base product.

685 parts by weight of commercial red lead are thoroughly mixed with 160 parts by weight of flowers of sulfur, the quantities named being the molecular proportions of the two materials, and corresponding to 81.1% of the red lead and 18.9% of sulfur. The red lead should preferably be a pure grade of red lead, such as is manufactured commercially on a large scale for the manufacture of storage battery plates and like uses. The intimate mixture of red lead and sulfur is next pressed firmly into a suitable vessel, cylindrical aluminum vessels being particularly satisfactory for this use, and the mixture being preferably pressed by means of a hydraulic or equivalent press in order to obtain a suitably high density, a pressure of about 500 kilos per square centimeter giving satisfactory results.

The base mix, prepared as above, is next heated to its temperature of ignition, when a reaction begins and progresses through the mixture, the red lead uniting with part of the sulfur to form lead sulfide, and part of the sulfur volatilizing. The product re-

maining after this treatment is a silvery mass consisting of lead sulfide admixed with some partly reduced lead oxide, and smaller amounts of lead sulfate and other compounds.

Preparation of base tablets.

The base mix resulting from the above treatment is crushed and sieved through a sieve having openings ¼ mm. square, all of the material being crushed until it will pass through a sieve of this fineness. The sieved product is next formed into tablets or pellets in any suitable press. The properties of the finished detector are in some measure determined by the density to which the tablets are pressed, and I prefer to press my tablets to a density corresponding to a specific gravity of 6.0.

Sensitizing of base tablets.

The tablets made as above are preferably heated to a temperature of 800° C. for two minutes, in an atmosphere consisting of 20 parts by volume of carbon bisulfide vapor and 80 parts by volume of sulfur dioxide gas. Super-atmospheric pressure may be employed to advantage, but very satisfactory results are obtained by the use of normal atmospheric pressures only. The tablets are allowed to cool in the atmosphere of sulfur dioxide and carbon bisulfide until quite cold, when they are removed from the treating vessel, and are ready for use. Instead of simultaneously treating the tablets in an atmosphere of carbon bisulfide vapor and sulfur dioxide gas in equilibrium, the tablets may be exposed to carbon bisulfide vapor alone or may be alternately exposed to an atmosphere of one reagent, and then the other, until the desired degree of sensitization has been brought about, although in general exposure of the tablets to the mixture of the two reagents under equilibrium conditions at the temperature employed gives equally satisfactory results, and represents a simpler procedure.

The process as described above may be modified in many respects, in accordance with the exact conductivity characteristics desired in the finished product. When a metal such as copper is used instead of lead, or when an element of the sulfur group such as selenium is used instead of sulfur, the effect is in both cases to increase the electrical conductivity of the resulting products. The use of a low pressure in the making of the tablet, or the use of a high proportion of sulfur dioxide in the final sensitizing step, has the reverse effect, and tends to decrease the electrical conductivity of the finished tablet. The electrical resistance of the tablet, as well as the rectifying effect, is also influenced by the time of heating in the final sensitizing step, and by the temperature employed, temperatures lower than 700° C., or a time of treatment of less than one minute tending to give products of high resistence and low rectifying effect. Increasing the time of treating the tablets in the sensitizing step, in an atmosphere of sulfur dioxide gas and carbon bisulfide vapor tends to give somewhat increased rectifying effect with good electrical conductivity, the period of treatment being capable of being extended to many times the normal treating period of two minutes, but a long time of treatment at a high temperature should be avoided, as this results in internal changes in the tablet, with the final result of the surface becoming rough and the rectifying characteristics being somewhat impaired.

The effects produced by the application of my present invention are not surface effects which influence only the extreme outer surface of my rectifying elements and current modifying devices, but appear to be true modifications of the fundamental or basic electron lattice of the material, the increase in rectifying ability, sensitiveness, and conductivity resulting from the practice of my invention extending throughout the entire substance of the mass of material being treated, and being by no means a surface phenomenon or confined to the outer layers of the material.

Instead of lead sulfide I may employ other metallic sulfides in the practice of my invention, the sulfides of such metals as bismuth, molybdenum and copper giving particularly satisfactory results. My invention is not limited to metallic sulfides however, as it may also be applied to the binary compounds of metals with other elements of the sulfur group than sulfur, the selenides and tellurides being in general the most satisfactory. I also wish to particularly point out that although I have referred specifically to gaseous electron-emitting and electron-absorbing reagents, I do not wish to be confined to reagents in the gaseous phase, as liquid reagents of suitable electron-emitting and electron-absorbing properties may be used, or the use of reagents may be replaced by the actual emission and absorption of electrons directly, by employing anodic oxidation and cathodic reduction in a suitable electrolytic cell. My invention is most conveniently applied by the use of gaseous electron-emitting and electron-absorbing agents existing together under equilibrium conditions, and I find the process as outlined in detail, suitably modified in accordance with the chemical nature of the material being treated and the reagents employed, to be in general the most satisfactory means of applying my invention, as it gives products of high sensitiveness in a minimum number of operating steps.

As an electron-emitting reagent either in the treatment of metallic oxides or metallic sulfides I prefer to use carbon bisulfide, and by the use of this reagent alone I can produce a high degree of sensitization in metallic sulfides. As an electron-absorbing reagent I prefer to use sulfur dioxide, or preferably a mixture of sulfur dioxide and a material having a chemically reducing action. In general, instead of employing pure carbon bisulfide as an electron-emitting agent and pure sulfur dioxide as an electron-absorbing reagent, I prefer to employ an equilibrium mixture of these two materials. A mixture of equal parts by weight of the two reagents give quite satisfactory results in the treatment of base-mix tablets of lead sulfide prepared by the reduction of lead oxide or other compound of lead by means of sulfur, but for this purpose I prefer to use a mixture of 80 parts by volume of gaseous sulfur dioxide and 20 parts by volume of vaporous carbon bisulfide, although as has already been pointed out, the proportions of these two reagents (or their equivalents when other classes of compounds than sulfides are being treated) may be varied within wide limits according to the exact properties desired in the final reaction product, and I have successfully made current rectifying devices by the treatment of the reaction product of red lead and sulfur, using a reagent of the type described in the sensitizing step, using all proportions of the electron-absorbing and the electron-emitting reagents within the range from pure carbon bisulfide to almost pure sulfur dioxide containing only a trace of carbon bisulfide, the exact proportions influencing the characteristics of the finished product however, and the most desirable results being obtained by the use of a mixture containing sufficient carbon bisulfide vapor to have relatively strong reducing properties under the temperature conditions prevailing in the sensitizing step.

In general I find that in the process of sensitization according to my present invention, the presence of free oxygen is a disadvantage, and accordingly it is best to exclude from the treating vessel not only pure oxygen and all air but also all materials which by reaction under the conditions existing in the treating chamber can give free oxygen. I also find that water vapor tends to act disadvantageously, and both moisture and substances which will react to give water vapor should be excluded from the treating vessel. I also find that it is advantageous to avoid diluting my reagents by the presence of admixed nitrogen or other inert gas, the best results being obtained from the use of the pure vapor of carbon bisulfide and pure gaseous sulfur dioxide, or an equilibrium mixture of these two materials in some suitable proportion, such for example as 80 parts by volume of sulfur dioxide and 20 parts by volume of carbon bisulfide. In the practice of my invention I find that porous masses of lead sulfide give the highest degree of sensitization and I prefer to use porous tablets made as described in my pending applications S. N. 615,160 and S. N. 617,841 as the raw material for my sensitization step, or equivalent material made as described in this application.

My invention is of very broad application and is by no means limited to the specific embodiment which I have described in detail for the purpose of illustration. Instead, my new process may be applied in many ways, and in general I may treat by my present invention a wide variety of metallic sulfides, selenides, tellurides and other compounds of a metal and a metalloid for the purpose of modifying their current conducting characteristics by the addition or withdrawal of electrons while maintaining the products being treated under suitable conditions of chemical reactivity through the application of an elevated temperature. I find that such products as have been described in my pending applications S. N. 615,160, S. N. 617,173, S. N. 617,841, S. N. 619,033, S. N. 621,112, S. N. 621,945 and S. N. 623,547 may be treated by my present invention, and that the light-sensitive and the current rectifying properties of these and other materials may be modified by the application of the process or method herein described. It should be understood that a wide variety of equivalents may be employed, without departing from the spirit of my invention of modifying the electrically conducting properties of metallic sulfides or equivalent materials by exposing them to electron-emitting or to electron-withdrawing agents, or simultaneously exposing such materials to a mixture of an electron-withdrawing and an electron-emitting reagent capable of existing together under equilibrium conditions, and that accordingly no limitations should be imposed in connection with my present invention except such as are indicated in the appended claims.

I claim:

1. The process of modifying the electrical conductivity of a compound of a metal and an element of the sulfur group which comprises heating such compound in the presence of carbon bisulfide.

2. The process of increasing the sensitiveness to ether waves of a compound of a metal and an element of the sulfur group which comprises heating such compound in the presence of carbon bisulfide.

3. The process of increasing the current rectifying characteristics of a compound

of a metal and an element of the sulfur group which comprises heating such compound in the presence of carbon bisulfide.

4. The process of increasing the current rectifying properties of a metallic sulfide which comprises heating such sulfide in the presence of carbon bisulfide.

5. The process of modifying the electrical conductivity of a metallic sulfide which comprises heating such sulfide in the presence of a carbon compounl of sulfur.

6. The process of modifying the electrical conductivity of a metallic sulfide which comprises heating such sulfide in the presence of a mixture of a carbon compound of sulfur and an oxygen compound of sulfur.

7. The process of modifying the electrical conductivity of a metallic sulfide which comprises exposing such sulfide at an elevated temperature to the presence of two compounds of sulfur of different composition.

8. The process of modifying the electrical conductivity of a metallic sulfide which comprises heating such sulfide in the presence of an oxygen compound of sulfur.

9. In the modifying of the electrically conducting characteristics of a metallic sulfide the process which comprises exposing the sulfide to an atmosphere containing both carbon bisulfide and sulfur dioxide.

10. The process of treating a compound of a metal and an element of the sulfur group which comprises exposing such compound to a mixture of gaseous sulfur dioxide and vaporous carbon bisulfide at a temperature in excess of 500° C.

11. The process of increasing the rectifying ability of a compound of a metal and an element of the sulfur group which comprises exposing such compound to a mixture of a reducible and an oxidizable compound of sulfur at a temperature in excess of 500° C.

12. As a step in the preparation of current modifying devices, the process which comprises exposing a metallic sulfide to an atmosphere containing substantially pure sulfur dioxide.

13. As a step in the preparation of current modifying devices, the process which comprises exposing a porous mass of a metallic sulfide to an atmosphere containing substantially anhydrous sulfur dioxide.

14. As a step in the preparation of current modifying devices, the process which comprises exposing a porous mass of metallic sulfide to an atmosphere containing sulfur dioxide.

15. As a step in the preparation of current modifying devices, the process which comprises exposing a metallic sulfide to an atmosphere containing one or more compounds of sulfur and substantially free from non-sulfur-containing gases.

16. As a step in the preparation of current modifying devices the process which comprises contacting a compound of lead with a gaseous mixture of carbon bisulfide and sulfur dioxide.

17. In the preparation of current rectifying products, the step which comprises heating a metallic sulfide in the presence of a reagent comprising sulfur dioxide and carbon bisulfide.

18. In the modifying of the electrically conducting characteristics of a compound of a metal and an element of the sulfur group, the process which comprises exposing the compound to an atmosphere containing an oxidizing ingredient and a reducing ingredient in balanced relationship.

19. In the modifying of the electrically conducting characteristics of a metallic sulfide the process which comprises exposing the sulfide to an atmosphere containing a compound of sulfur having reducing characteristics and a compound of sulfur having oxidizing characteristics.

In testimony whereof, I have hereunto subscribed my name this 22nd day of September 1923.

WALTER O. SNELLING.