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COBALT SALICYLALDEHYDEETHYLENEDIIMINE AND METHOD OF PRODUCTION

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This invention relates to a new composition of matter, and more particularly, to a new allotropic form of cobalt salicylaldehydeethylenediimine, including methods for producing the same and methods of substantially continuously producing oxygen and nitrogen cyclically from the atmosphere therewith.

There exist systems by which oxygen may be selectively absorbed from the air under certain conditions and then regenerated as substantially pure oxygen by a suitable change of conditions leaving the system in a state such that a return to the original conditions will again allow oxygen absorption from air.

Artificially produced compounds having the desired characteristic of primarily absorbing and retaining and secondarily liberating the more or less loosely held oxygen have been made by treating various organic and even inorganic compounds under varying conditions of pressure and temperature first to form oxides and then to render the oxides so formed unstable, generally by increasing the temperature so as to drive off the oxygen as a gas.

Utilizing the method of this invention, a desired chemical, to wit: cobalt salicyladehydeethylenediimine, hereinafter referred to as CoSaEn, is first combined with a blocking agent which upon removal under suitable conditions leaves chemical bonds which may then act to take up oxygen from the air with a rapidity varying within limits inversely with the temperature and directly with the pressure. The oxygen is then given up with a rapidity and ease dependent upon a reversal of the foregoing conditions.

It is not here intended to review the manifold processes which have been heretofore used to achieve a compound of the character described, nor is it intended to catalog the various compounds which have been found to be suitable in greater or lesser degrees for the purposes contemplated. We merely intend to indicate that many costly and elaborate attempts have been made to obtain improved chemical compounds of constantly greater efficiency for use in the separation of oxygen from the air.

Heretofore it has not been possible to chemically generate oxygen in any manner which is capable of competing with mechanical methods on favorable economic terms. It has generally proven more practical, therefore, to obtain commercial oxygen through fractionation of liquid air or electrolysis of water in spite of the fact that such methods require a large investment of

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capital and result in the necessary construction of relatively large units of equipment.

Commercial processes demand that a chemical intended for use as contemplated must be capable of reversibly and rapidly absorbing a significant fraction of its own weight of oxygen, and its value for such use will obviously be measured by its success in these respects. Moreover, it is necessary that the chemical compound finally determined upon be composed of readily obtainable ingredients whose cost will bear a reasonable relationship to the value of the product obtained.

The form of the compound to which this invention relates will rapidly and efficiently absorb approximately 4.9% of its own weight of oxygen within low temperature and pressure ranges. In addition, it is estimated that approximately 1.5 lbs. of oxygen may be stored per cubic foot of necessary equipment. The liberated oxygen gas may escape from the compound with a force equal to a pressure of several atmospheres under easily obtainable conditions.

While presently known less efficient solutions are active to absorb and liberate oxygen within the contemplated temperature ranges hereinafter set forth, solids analogous to those of the instant invention have required temperatures ranging from 400 to 800 degrees C. for said purposes, except as hereinafter noted.

It is therefore an object of this invention to provide a new and improved chemical compound having the desired characteristics described and which is capable of continuous cyclic absorption and desorption of a greater percentage of oxygen by weight than has been heretofore obtainable.

Another object is to provide a new and improved chemical compound by means of which oxygen may be rapidly and efficiently generated from the atmosphere.

Another object is to provide a new and improved chemical compound which can compete commercially with conventional mechanical apparatus, particularly in relatively small unit installations.

Another object of this invention is to provide a new and improved regenerative chemical compound which, in solid, preferably granular form, is capable of cyclically and continuously taking up and liberating oxygen from the atmosphere at temperatures ranging from approximately 0 degrees centigrade to approximately 130 degrees centigrade over long periods of time without substantial degeneration or loss of efficiency.

A further object is to provide a solid regenerative chemical of new and improved granular form

which can continuously and alternately absorb and desorb atmospheric oxygen at various pressures ranging from less than one to several atmospheres and in a temperature range of from 0 degrees C. to 130 degrees C.

Another further object is to provide a chemical compound usable for the purposes stated, the formula of whose oxygenated form, sometimes referred to herein as the oxide or the oxidized form, is $(C_{16}H_{14}O_2N_2Co)_2O_2$ and whose real density is approximately 1.6.

Yet another object is to provide a cobaltous chemical compound having the desirable characteristic herein set forth, whose oxygenated form contains one molecule of O_2 for every two atoms of cobalt present in said compound and which can alternately release and reabsorb substantially all of the theoretical amount of oxygen in its oxide under the influence of readily variable and easily obtainable pressure and temperature changes, said compound being capable of withstanding a substantially indefinite number of such cycles without poisoning or substantial deterioration, under suitable conditions.

It is more specifically an object to create a more efficient form of cobalt salicylaldehydeethylenediimine, of the general formula

$$C_{16}H_{14}O_2N_2Co$$

than any heretofore known for the purposes herein set forth, said compound having an orthorhombic cell structure and a coplanar stereochemical form in its solid state.

A still further object is to provide a commercially practicable method of producing the desired form of cobalt salicylaldehydeethylenediimine herein described.

Another further object is to provide a commercially suitable method and apparatus for the continuous generation of oxygen from the atmosphere and/or nitrogen by subtraction.

It is also an object to improve prior art compounds, methods, and apparatus, intended to accomplish a similar purpose.

Other objects and purposes will appear and be more clearly set forth in the following description considered in the light of the appended claims.

Preliminarily, we desire to set forth one example of a preferred procedure for obtaining our desired compound.

In said example 164 grams of 67.9% aqueous ethylenediamine was dissolved in 6.5 liters of commercial ethyl alcohol. To the resultant mixture was added a solution of 576 grams of cobalt acetate, or its equivalent in the form of cobalt chloride and sodium acetate, in 2.9 liters of water. To this solution, either at room temperature or at some higher temperature up to 60 degrees C., was added 576 grams of salicylaldehyde. The order of mixing above set forth is merely demonstrative and may be varied in a manner well known to those skilled in the art.

As the last ingredient, salicylaldehyde, was added, the vessel containing the above-mentioned ingredients was closed off and placed under a vacuum pump to remove oxygen from the solution. Said solution was permitted to set for two or three minutes, at the end of which time it appeared as a brown-red gel. Said gel was allowed to stand at room temperature for five or six days during which time it slowly crystallized. It was found that the crystallization time could be cut to less than one day be retaining the gel above normal room temperature, but the accelerated procedure resulted in smaller crystals.

In either case, whatever crystallization time was used, the resultant crystals were of an inactive form of CoSaEn, which would not take up oxygen even though subjected to a pressure of 2,000 lbs. per square inch and a temperature of 180 degrees C.

As the next step in the preparation of CoSaEn in its active most desired form, the inactive crystals were dissolved in pyridine in the ratio of three grams of pyridine to one gram of the inactive material, and the resultant solution was refluxed for approximately two hours, then preferably cooled, as in ice or salt ice, to room temperature and caused to recrystallize at said temperature. The crystals so formed were filtered in the absence of air, washed with ether and then dried, thereby providing a compound having one molecule of pyridine per atom of cobalt.

These monopyridinate crystals were next heated at a temperature of approximately 160 degrees C. in a preferably rapid stream of air to bring about depyridination, i. e., the removal of the pyridine. The resultant crystalline compound, active to absorb oxygen at readily available temperatures and pressures, was CoSaEn in its most active form, and in its oxygenated state contained one molecule of oxygen for each two atoms of cobalt.

It was found that the actual useful activity of this most active form of CoSaEn was within 97% to 99% of its theoretical capacity to absorb and release oxygen reversibly as defined by its formula. The real density of the material as produced was approximately 1.6. In its powdered state, its density was approximately .3 to .8 depending upon the method of preparation of the powder. It is preferable, however, to compress the material into a cakelike mass and then to break or to crush the cake into the form of small pellets having about three or four times the density of the powder. Such a granular form of the material is generally somewhat porous and takes up oxygen as readily as the powdered form, but is more convenient and practical in use.

In order to verify the actual as compared to the theoretical oxygen-carrying and effective oxygen-generative properties of the most desired form of the material, exhaustive tests were made of which the following example is illustrative:

Wt. of sample after driving off oxygen at 100 degrees C.: 2.369 gm.
Wt. of sample after exposure to oxygen gas: 2.486 gm.
Wt. of oxygen absorbed: .117 gm. or 4.94%
Wt. of sample after oxygen again driven off: 2.369 gm.
Wt. of oxygen driven off: .117 gm. or 4.94%

It will be seen from the above description that a chemical may be prepared having bonds closed by pyridine molecules. In this condition the material can be crystallized. After crystallization has taken place, the pyridine can be removed without causing any major change in molecular arrangement, and there are then spaces available for the attachment of oxygen. Thus, the pyridine can be broadly called a blocking agent, which permits the final preparation of the crystalline material to the end that when this blocking agent is subsequently removed by the application of heat, the organic structure becomes active and is able to take up and give off oxygen in accordance with the temperatures and pressures supplied to the material, most desirably at preferred values later set forth.

While pyridine is herein used to illustrate the employment of a blocking agent, it is intended to be merely illustrative of blocking agents in general which perform a similar function and which, when removed from the ultimately desired compound, act to liberate bonds for the attachment of oxygen. Thus the most preferred form may also be obtained by rapid precipitation from neutral aqueous solutions in lieu of pyridine, in which case the blocking agent is a water molecule. Other blocking agents which have been used are piperidine, ethyl alcohol, and propyl alcohol.

As an alternative and even more preferable and efficient method of achieving the most desired form, the whole operation may be performed in one step to directly produce the monopyridinate. This may be done by mixing, in aqueous solution, suitable proportions of the ingredients hereinabove mentioned, to wit: ethylenediamine, cobaltous chloride, and sodium acetate, (or the equivalent: cobalt acetate), salicylaldehyde and (preferably lastly) a quantity of pyridine preferably corresponding to at least two molecules of pyridine per atom of cobalt. By this procedure, the use of alcohol is obviated and the step of recrystallizing from pyridine is also eliminated. The ingredients of the desired CoSaEn compound may be mixed in propyl alcohol to obtain a gel which after drying itself weakly holds propyl alcohol molecules. The removal of these propyl alcohol blocking molecules by heating in air at a temperature of approximately 100 degrees C. again produces the most active form of crystalline CoSaEn.

It appears desirable to note that the several forms of the compound, while in some instances expressible by the same chemical formula, are widely different not merely in their ability to absorb oxygen but also in their other physical properties. It has hitherto been well known that independent allotropic forms of the same general chemical compound may exist although the existence of one commonly known form does not furnish adequate data upon which to predict the existence of any other form. Thus, for example, diamond, graphite, and amorphous carbon are all expressible by the same chemical formula or symbol "C," and chemically may be deemed identical. It is obvious, however, that while accidentally of the same empirical formula, these forms are widely different and possess utterly distinct properties and uses. Thus diamond may be used for grinding and cutting, while graphite may be used as a lubricant or refractory. Neither diamond nor graphite, on the other hand, can function as an adsorbent in the manner of charcoal. These three forms of carbonaceous material possess other physical differences, into the details of which it is not deemed pertinent to examine at this time except to note and underscore the fact that the mere accident of similarity of chemical expression of a compound as compared with other compounds does not necessarily establish the physical identity and equivalence of said forms. Similarly, there are several allotropic forms of chemical substances differing in chemical and physical properties, but each describable as cobalt salicylaldehydeethylenediimine.

As stated, the form is unaffected by the method of creating the desired form of CoSaEn as by its said crystallization directly from pyridine or other solvents whether or not the blocking agent employed is restricted to pyridine.

Yet another less active form of CoSaEn is known to exist which in its oxygenated state contains one molecule of oxygen per three cobalt atoms, corresponding to approximately 3.5% of oxygen in the oxide. The molecular geometry and crystalline structure of the compound is different from the active forms of CoSaEn heretofore discussed, and the formula of the oxide is $(C_{16}H_{14}O_2N_2Co)_3O_2$. Moreover, the color of this known form of CoSaEn is red-brown, the cell structure triclinic, and the configuration of the molecule is said to be octohedral. Said configuration is in contrast to the coplanar configuration of the preferred form of CoSaEn in its most active state as determined by X-ray and magnetic analysis. Moreover, the preferred form of CoSaEn is brown in color and possesses an orthorhombic cell structure.

X-ray analysis of the three forms of CoSaEn hereinabove referred to is summarized in the following table:

	Inactive Form	Less active Form	Preferred Form
a	14.07	6.6	6.70
b	7.06	11.9	7.97
c	26.25	12.6 or 25.2	25.90
	Monoclinic	Triclinic	Orthorhombic

The preferred most active CoSaEn compound may also be utilized for the generation of oxygen while in pyridine solution. When utilized in this manner, the solution may be circulated between high and low temperature baths associated with a proper pressure control of admixed air in such a manner that pyridine is released and oxygen taken up, the pyridine and oxygen being separately trapped and the pyridine caused to return to the solution as a part of the generative cycle. Thus it may be seen that the use of our compound is capable of much variation, and it is not intended to limit the utilization thereof to any particular method.

Referring now briefly to a preferred mode of use of CoSaEn in its most active and preferably granular form, the granules may be placed in any number of suitable containers, such as tubes, which may be positioned in a heat exchanger and the granules held in place by a porous packing material in a manner to permit air to pass through the tubes and through or over the granules at any desired pressure. For this purpose the tubes may be connected to the atmosphere through any desired pressure and/or vacuum pumps by way of suitable pipe and valve systems, all in a manner well known to those skilled in the chemical or mechanical arts.

In addition appropriate connections may be made so that cooling and/or heating agents (such as water and steam) may alternately be conducted into the heat exchanger for circulation around and between the tubes to alternately cool or heat the tubes and their contents as desired. Waste outlets may also be connected to the tubes for removing any oxygen-depleted air from around the active CoSaEn material.

It has been found preferable to cool the inlet air to approximately 20 degrees C. before its passage through the tubes, and initially to provide an excess of air over what the active material can theoretically take up at the established pressure.

After passing the cooled air over the active material for a length of time sufficient to permit

it to absorb such a percentage of oxygen as will make an efficient absorption cycle, the heat exchanger may be discharged of the tap water and charged with steam to obtain a tube temperature of approximately 100 degrees C. Thereby the absorbed oxygen will be caused to escape from the active material in the tubes under several atmospheres of pressure whence it may be conducted to a place of storage or use.

Obviously, a continuous productive cycle of oxygen absorption and desorption can thus be set up, the CoSaEn alternately absorbing oxygen from the air at relatively low temperatures and high pressures and giving up the oxygen under conditions of relatively low pressures and high temperatures.

The oxygen desorption at 100 degrees C. is smooth and rapid and can be efficiently accomplished in from three to five minutes. The absorption time, as will be seen later, can be reduced to ten minutes, if desired, with about 85% recovery. Usually the absorption time will determine the period of a complete absorption-desorption cycle, as the desorption time is less than the absorption time for efficient recovery at the lower absorption pressures. Thus, a complete cycle, if desired, can be easily reduced to as little as fifteen minutes, including the heating and cooling of the interchanger.

While the dynamics and kinetics of our process will vary somewhat in accordance with the type of heat interchange apparatus used, and the quality and quantity of materials used, the following table may be taken to be representative of the performance of a unit quantity of material in a tubular heat interchanger of the general type described. The absorption temperature in all cases cited is approximately 20 degrees C., and the desorption temperature in all cases cited is approximately 100 degrees C. The oxygen given off was measured in an ordinary gas meter and the desorption time was approximately five minutes in each case. The column of figures below entitled "Percent recovery" is based upon the maximum amount of oxygen which could be obtained from the unit quantity of CoSaEn after passing oxygen gas through the unit quantity for one hour, and corresponds to a material having 94% of the theoretical activity.

Air Pressure	Time	Volume of Air passed through Cubic Feet	O_2 Percent Recovery
	Hours		
20	1	15	86
40	1	15	96
40	½	8	88
80	½	8	98
80	¼	4	92

If it is desired to still further cut down the absorption time, the pressure can be raised to 90 pounds, for example, and applied for ten minutes with 10% excess air to give an 85% recovery. Still higher pressures still further reduce the absorption time.

The rate of O_2 production per unit weight of active material is greater when operating on the shorter periods. It will be seen that two fifteen-minute periods at 80 pounds air-pressure will give 184% recovery, whereas three ten-minute periods at 90 pounds air-pressure will give 255% recovery. This shortening of the absorption time, however, is clearly limited by the time required to heat and cool the material of the heat exchanger. It has been found, however, that a 15-minute cycle is practical and economical for commercial production of O_2.

We have found that the pressure of oxygen over an oxygenated sample of the compound is about 55 millimeters of mercury at room temperature (22 degrees C.), one atmosphere at about 58 degrees C., and about six atmospheres at 100 degrees C. The material provides, therefore, sufficient delivery pressure for some practical uses and therefore may be stored without pumping at six atmospheres or less when the 100 degrees C. desorption temperature is utilized, and at higher pressures, if boosted by a pump or compressor. Obviously, however, if the delivery pressure can be less, as for example one atmosphere, the desorption temperature need only be about 60 degrees C. Therefore higher temperatures can be used to provide higher output pressures.

It can very readily be seen from the above figures that the uptake of oxygen can be controlled in accordance with the applied temperature and pressure, and that the release of oxygen can be controlled in accordance with the amount of heat applied to the material. It is not, of course, necessary to use a temperature range of from 20 degrees C. to 100 degrees C. for the regenerative cycle inasmuch as lower, higher, or intermediate temperatures can be utilized in accordance with individual conditions desired. However, it is believed that the figures given herein will readily make apparent to all those skilled in the art, the manner by which this invention may be applied to any particular problem involving the store and subsequent release of oxygen.

Experiments have been made to determine whether or not the active material is deteriorated by repeated cyclic action thereof. Careful measurements have been made over a large number of cycles performed under controlled conditions, and no appreciable differences could be detected between the action of the material at the end of a single run, and the performance thereof at the beginning of the run. No poisoning occurred but the material could be used to produce approximately 20 lbs. of O_2 per pound of CoSaEn before a 50% reduction of its operative efficiency per cycle occurred. Crystallized CoSaEn does not react with water at room temperature at any appreciable rate, and while moist air can be used through the material, it is desirable to exclude moisture as far as possible without undue multiplication of equipment or expense. At high temperatures, however, prolonged exposure to steam and oxygen may result in the reversion of the material to an inactive, inert cobaltic compound; but such an exposure can be readily guarded against, and could not take place except by accident.

While we have described our process so far as being applicable to the selective absorption of pure oxygen from the air, it is obvious that substantially the same general type of apparatus can be utilized to selectively absorb oxygen from a mixture of gases. However, when our process is utilized for the selective absorption of oxygen from atmospheric air, it will be obvious that the air that has passed through the heat exchanger, as above described, has had a large percentage of its oxygen removed from it. The percentage of nitrogen remaining in the output air is therefore high.

Reference to a "molecule" of oxygen in this

specification and claims is intended to denote one molecule of oxygen consisting of two atoms.

The gist of this invention is the production of a new form of CoSaEn and the alternate and continuous absorption and desorption of atmospheric oxygen therewith.

Although we have herein described our invention and its mode of production, application and use in what we deem to be its most preferred mode and form, departures may be made therefrom without departing from the spirit of the invention as expressed in the appended claims.

Having thus described the invention what is claimed as new and desired to be secured by Letters Patent is:

1. The formation of a preferred allotropic crystalline form of cobalt salicylaldehydeethylenediimine in its non-oxygenated state by the steps of combining aqueous ethylenediamine, ethyl alcohol, cobalt acetate, water and salicylaldehyde in the absence of air to form a gel; crystallizing said gel; dissolving the resultant crystals in a solution comprising a blocking agent selected from the group consisting of propyl alcohol and pyridine; recrystallizing said dissolved material; filtering, washing and drying the recrystallized material in the absence of air to form crystals containing said blocking agent; and removing said blocking agent by heating said recrystallized material to an elevated temperature is a stream of air to preclude combination of oxygen therewith.

2. The formation of a preferred allotropic crystalline form of cobalt salicylaldehydeethylenediimine in its non-oxygenated state by the steps of combining aqueous ethylenediamine, ethyl alcohol, cobalt acetate, water and salicylaldehyde in the absence of air to form a gel; crystallizing said gel; dissolving the resultant crystals in a solution of pyridine; recrystallizing said dissolved material from said pyridine solution; filtering, washing and drying the recrystallized material in the absence of air to form monopyridinate crystals; and depyridinating said monopyridinate crystals by heating said crystals in a stream of air at approximately 160 degrees centigrade so as to preclude combination of oxygen with said crystals.

3. The formation of a preferred allotropic crystalline form of cobalt salicylaldehydeethylenediimine in its non-oxygenated state by the steps of combining aqueous ethylenediamine, ethyl alcohol, cobalt acetate, water and salicylaldehyde; removing oxygen from said mixture in the absence of air to form a gel; crystallizing said gel; dissolving the resultant crystals in a solution comprising propyl alcohol; recrystallizing said dissolved material from said alcohol solution; filtering, washing and drying the recrystallized material in the absence of air to form said cobalt salicylaldehydeethylenediimine combined with propyl alcohol; and removing said propyl alcohol by heating the crystals at approximately 100 degrees centigrade in a stream of air to preclude the combination of oxygen with said cobalt salicylaldehydethylenediimine.

4. The method of producing a preferred active form of cobalt salicylaldehydeethylenediimine comprising mixing ethylenediamine, salicylaldehyde, a cobaltous salt and pyridine in aqueous solution to crystallize therefrom cobalt salicylaldehydeethylenediimine combined with the pyridine, and separating said pyridine from said cobalt salicylaldehydeethylenediimine by heating at approximately 160 degrees centigrade in a stream of air to preclude the combination of oxygen therewith.

5. A chemical compound of orthorhombic cell structure in its non-oxygenated form, whose molecular measurement is approximately *a.* 6.70, *b.* 7.97, *c.* 25.90, whose empirical formula is $C_{16}H_{14}O_2N_2Co$, and which combines with oxygen according to the formula $(R)_2O_2$ where R is $C_{16}H_{14}O_2N_2Co$ having a valence of 2.

6. The method of forming a brown orthorhombic, coplanar, crystalline form of cobalt salicylaldehydeethylenediimine, having cell dimensions as follows: *a* equals 6.70, *b* equals 7.97, and *c* equals 25.90; comprising the steps of combining ethylenediamine, salicylaldehyde, a cobaltous salt and pyridine in aqueous solution to crystallize therefrom cobalt salicylaldehydeethylenediimine combined with the pyridine, and heating said crystals in a stream of air at approximately 160 degrees centigrade.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,091,023	Sinding-Larsen	Mar. 24, 1914
1,117,352	Ehrlich	Nov. 17, 1914
2,188,746	Bersworth	Jan. 30, 1940
2,217,850	Warne	Oct. 15, 1940

OTHER REFERENCES

Pfeiffer et al., "Annalen der Chemie," vol. 503 (1933), pages 125–126.

Calvin et al., "J. Am. Chem. Soc.," vol. 68, (Nov. 1946), pages 2254–2256.

Tsumaki—Bull. Chem. Soc. of Japan, vol. 13, 1938, pages 252–260, 379–591.