

- [54] **ABSORPTION PROCESS FOR PRODUCING OXYGEN AND NITROGEN AND SOLUTION THEREFOR**
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- [21] Appl. No.: 393,711
- [22] Filed: Jun. 30, 1982
- [51] Int. Cl.³ B01D 19/00
- [52] U.S. Cl. 55/38; 55/43; 55/53; 55/68; 252/188.28; 252/181.7; 252/181.6
- [58] Field of Search 55/68, 38, 43, 45, 57, 55/48, 51, 53; 423/219, 579; 252/188.28, 181.7, 181.6

56-48243 5/1981 Japan 55/68

Primary Examiner—Bernard Nozick
 Attorney, Agent, or Firm—Chernoff, Vilhauer, McClung, Birdwell and Stenzel

[57] **ABSTRACT**

Process for the separation and purification of oxygen and nitrogen is disclosed which utilizes solutions of oxygen carriers to selectively absorb oxygen from a gaseous stream, leaving nitrogen as a byproduct. In the process, an oxygen carrier capable of reversibly binding molecular oxygen is dissolved in a solvent solution, which absorbs oxygen from an oxygen-containing gaseous feed stream such as atmospheric air and desorbs oxygen to a gaseous product stream. The feed stream is maintained at a sufficiently high oxygen pressure to keep the oxygen carrier in its oxygenated form during absorption, while the product stream is maintained at a sufficiently low oxygen pressure to keep the carrier in its deoxygenated form during desorption. In an alternate mode of operation, the carrier solution is maintained at a sufficiently low temperature and high oxygen pressure to keep the oxygen carrier in its oxygenated form during absorption, and at a sufficiently high temperature to keep the carrier in its deoxygenated form during desorption. Under such conditions, exceptionally high oxygen concentrations on the order of 95% to 99% are obtained, as well as a long carrier lifetime in excess of 3 months, making the process commercially feasible.

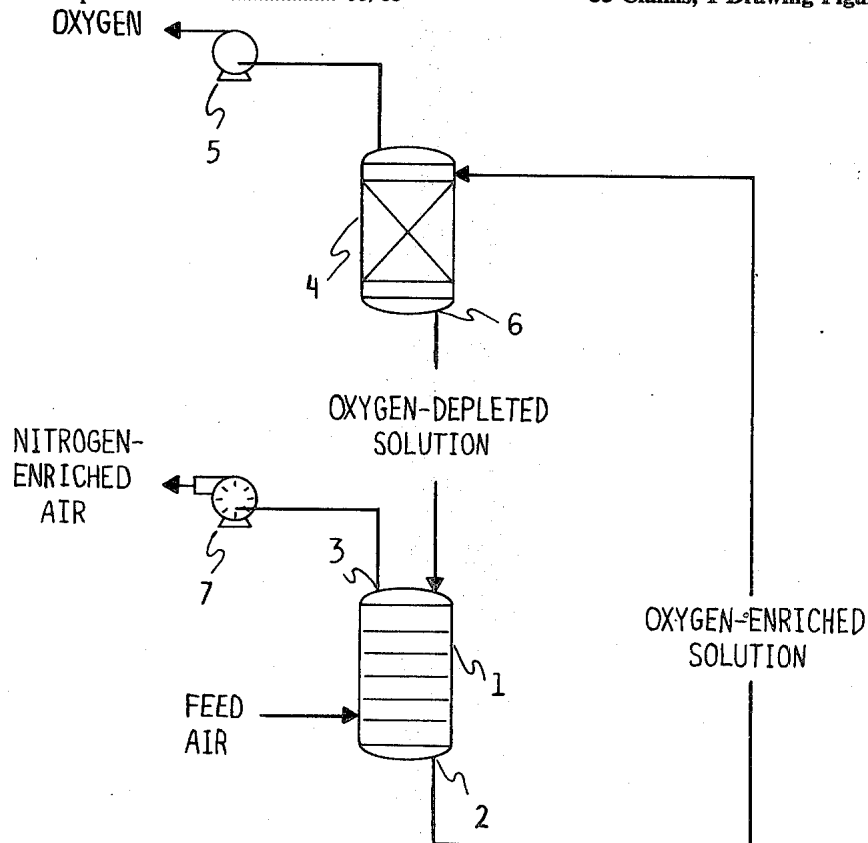
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35 Claims, 1 Drawing Figure



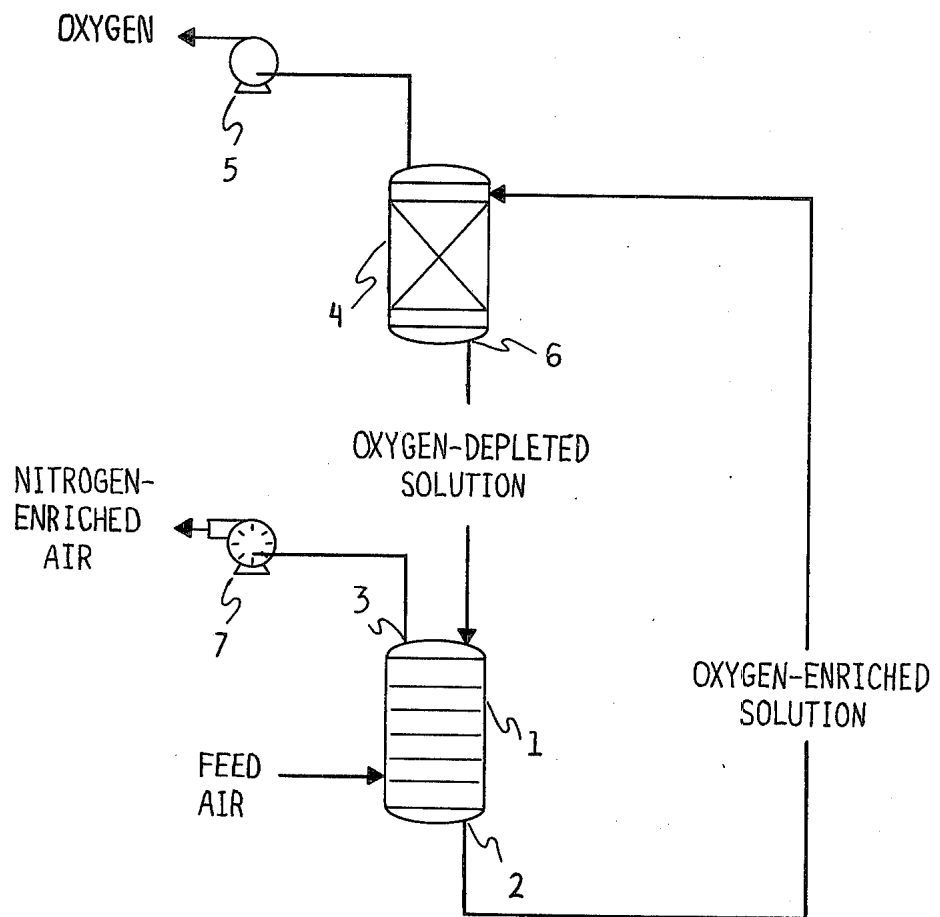


FIGURE 1

ABSORPTION PROCESS FOR PRODUCING OXYGEN AND NITROGEN AND SOLUTION THEREFOR

The government has rights in this invention pursuant to Contract No. DE-AC06-79ER10337 awarded by the U.S. Department of Energy.

BACKGROUND OF THE INVENTION

Oxygen and nitrogen are among the most widely used chemicals in the world, the annual consumption of each gas amounting to in excess of 20 million tons in the United States. Most of this oxygen is used in the steel industry and related metals manufacturing processes. Oxygen-enriched air has also found significant uses, including treatment of waste water, non-ferrous smelting, glass production, medical applications, and other chemical oxidation processes. In addition, there is a great potential market for oxygen-enriched air in the synthetic fuels industry. Nitrogen and nitrogen-enriched air are useful primarily for inert blanketing atmospheres and for refrigeration.

More than 99% of all oxygen and nitrogen is currently produced by cryogenic fractionation, or a process involving lowering the temperature of air sufficiently (to about -215°C .) to liquefy it and then using a multistage distillation process to produce pure oxygen and pure nitrogen. A major drawback of such cryogenic processes is that they require a great deal of en-

such as hydrocarbons, inert gases and oxides of sulfur and nitrogen that were present in the feed stream. PSA is economically competitive with cryogenic production of oxygen only in plant sizes up to perhaps 40 tons/day. Large-scale (100-3,000 tons/day) plants currently all use the cryogenic process.

It was observed by Tsumaki over 40 years ago in *Bull. Chem. Soc. Japan* 13 (1938) 252 that synthetic chelate-type compounds reversibly bind oxygen in the solid state. Subsequently, many researchers have investigated different chelate-type compounds in attempts to discover compounds that could be used to produce oxygen-enriched air. See, for example, the recent review by Jones, Summerville and Basolo in *Chem. Reviews* 79 (1979) 139. The most promising compound, commonly called fluomine,* has been studied for 35 years by the U.S. Air Force for potential use in providing breathing oxygen for crews of military aircraft. This compound is used to selectively bind oxygen at about 40°C . and 400 mmHg oxygen partial pressure, and releases oxygen at about 110°C . and 90 mmHg oxygen partial pressure. Fluomine is active in binding oxygen only in the solid state, and its activity is highly dependent on crystal structure. Furthermore, its useful operating lifetime is less than 10 days due to degradation of the fluomine at the elevated temperatures and pressures required for operation.

* N,N'-bis(3-fluorosalicylidene)ethylenediaminecobalt(II), described by Wilmarth, Aranoff and Calvin in *J. Amer. Chem. Soc.* 68 (1946) 2263, and by Adduci in *Chem. Tech.* 6 (1976) 575.

nitrogen- and/or oxygen-containing Lewis bases defined as "axial bases" unexpectedly enhance the ability of certain metal-containing complexes (carriers) to selectively, rapidly and reversibly absorb and desorb oxygen in solution to produce oxygen-enriched air. Said combinations and carriers (carrier solutions) provide greater selectivity and more extended lifetime than anything encountered or predicted in the prior art. Oxygen concentrations as high as 98.8% have been demonstrated, which is much higher than that for any reported adsorption process. These carrier solutions have shown continuous operation for over 100 days, or a full order of magnitude better than any similar process previously reported.

A further advantage of the present invention over the prior art is that, since oxygen is selectively removed from the feed stream rather than nitrogen, the oxygen-enriched air produced does not contain the argon or other impurities that are present in oxygen-enriched air produced by PSA.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the basic absorption and desorption modes and exemplary apparatus useful in the process of the present invention.

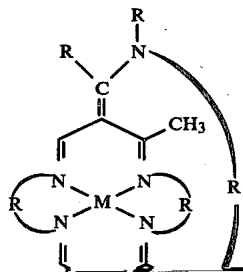
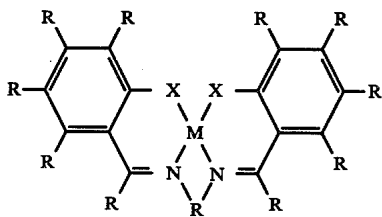
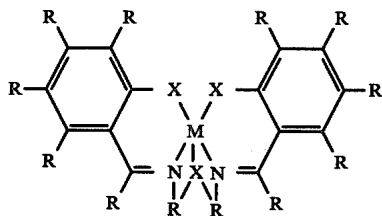
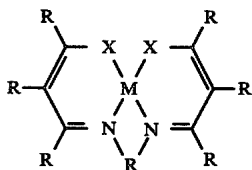
DETAILED DESCRIPTION OF THE INVENTION

The feed stream for the separation process of the present invention may be ordinary atmospheric air or other gaseous stream containing oxygen. Since, in the case of air, nitrogen is the only other primary component, the present invention is also useful for the recovery of nitrogen and nitrogen-enriched air. As schematically shown in FIG. 1, the feed stream is brought into contact with the carrier solution preferably in an absorber section 1 and preferably at substantially atmospheric pressure for economic reasons, but other pressures of the feed stream are also acceptable so long as the partial pressure of oxygen of the product stream in the stripper section 4 is at least approximately 10 mmHg

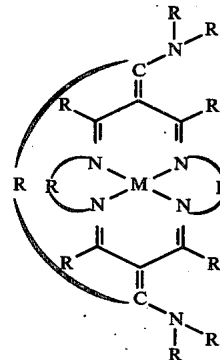
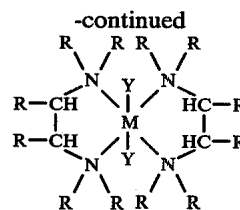
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carrier solution of the present invention. Such an axial base provides an additional coordinating atom to those contained in the oxygen carrier, which assists in the reversible binding of oxygen. Classes of axial bases found useful are imidazoles, ketones, amides, amines, sulfoxides, pyridines, and other Lewis bases containing secondary or tertiary nitrogen. Preferred examples include 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, dimethylsulfoxide, N,N'-diethylenediamine, 4-dimethylaminopyridine, 4-aminopyridine, pyridine, 4-methylpyridine, 4-methylaminopyridine, 3,4-lutidine, 3,5-lutidine, 4-cyanopyridine, 4-methoxypyridine, 4,4-bipyridine, pyrazine, and N-methylpyrazinium halides.

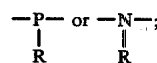
The oxygen carriers useful in the present invention may be described as metal-containing complexes containing the structure



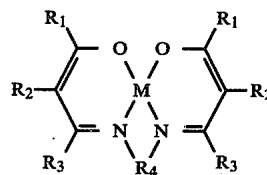
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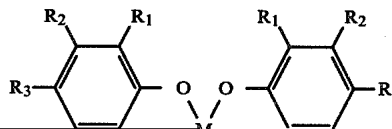
wherein M represents a metal such as cobalt, iron, nickel, copper, manganese, ruthenium, or rhodium; X is $-O-$, $-S-$,

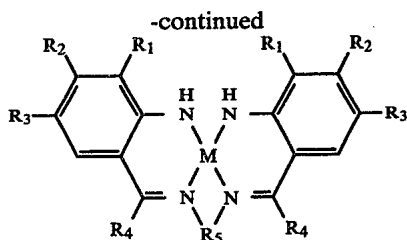


R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety; and Y represents a halide, nitrate, thio-cyanate, or cyanide anion. Preferred metals are cobalt(II) and iron(II). Successful carriers must exhibit rapid oxygenation and deoxygenation, must be readily soluble in solutions of the solvents and axial bases noted above, and must be stable to irreversible oxidation or other degradation. The carriers generally bind oxygen at sufficiently high oxygen pressures and sufficiently low temperatures, and they generally release the oxygen at sufficiently low oxygen pressures and sufficiently high temperatures. Classes of such carriers found useful include metal-containing complexes generally of the following structures:

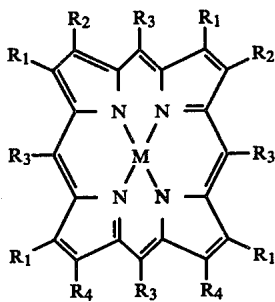


Bis(acetylaceton) ethylenediimine derivatives

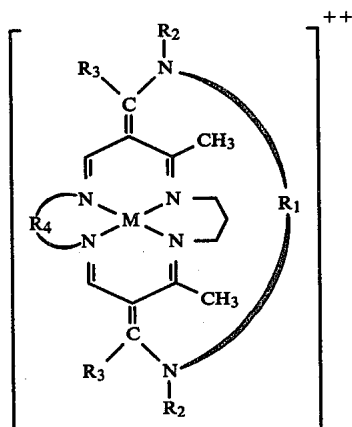




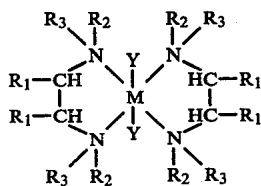
Bis(2-amino-1-benzaldehyde)-ethylenediimine derivatives



Porphyrin derivatives



"Dry-cave" complex derivatives



-continued

N,N'-substituted ethylenediamine derivatives

- 5 wherein M is the metal atom; the "R" groups represent hydrocarbon moieties with or without hetero-atoms, including alkyl groups, aryl groups, alkoxy groups, halides, or nitrogen-containing groups; and Y represents a halide, nitrate, thiocyanate or cyanide anion.
- 10 Specific examples include those shown in Tables I-IV, taken from a review by Jones, Summerville, and Basolo in *Chemical Reviews* 79 (1979) 139; those shown in Table V, described by Khare, Lee-Ruff and Lever in *Canad. J. Chem.* 54 (1976) 3424; those described by Stevens and Busch in *J. Amer. Chem. Soc.* 102 (1980) 3285; those described by Collman in *Accts. Chem. Res.* 10 (1977) 265; and those described by Almog, Baldwin, Dyer and Peters in *J. Amer. Chem. Soc.* 97 (1975) 226.

TABLE I

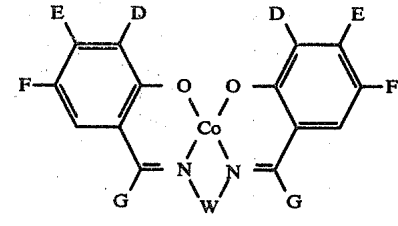
Compound	V	A	B
30 Co(acacen)	-(CH ₂) ₂ -	CH ₃	H
Co(Meacacen)	-(CH ₂) ₂ -	CH ₃	CH ₃
Co(Phacacen)	-(CH ₂) ₂ -	CH ₃	C ₆ H ₅
Co(benacen)	-(CH ₂) ₂ -	C ₆ H ₅	H
Co(Clbenacen)	-(CH ₂) ₂ -	p-ClC ₆ H ₄	H
Co(Brbenacen)	-(CH ₂) ₂ -	p-BrC ₆ H ₄	H
Co(Meobenacen)	-(CH ₂) ₂ -	p-CH ₃ C ₆ H ₄	H
35 Co(bensacen) ^a	-(CH ₂) ₂ -	p-CH ₃ OC ₆ H ₄	H
Co(Clbensacen) ^a	-(CH ₂) ₂ -	C ₆ H ₅	H
Co(Brbensacen) ^a	-(CH ₂) ₂ -	p-ClC ₆ H ₄	H
Co(Meobensacen) ^a	-(CH ₂) ₂ -	p-BrC ₆ H ₄	H
Co(sacacen) ^a	-(CH ₂) ₂ -	p-CH ₃ C ₆ H ₄	H
40 Co(sacacen) ^a	-(CH ₂) ₂ -	p-CH ₃ OC ₆ H ₄	H
Co(sacsacpn) ^a	-(CH ₂) ₂ -	CH ₃	H
	-(CH ₂) ₂ -	CH ₃	H
	-(CH ₂) ₂ -	CH ₃	H
45 Co(sacsactn)	-(CH ₂) ₃ -	CH ₃	H
Co(sacsacchxn)	-(CH ₂) ₂ -CH ₂ - (CH ₂) ₄	CH ₃	H

^aoxygen atoms are replaced by sulfur

TABLE II

Compound	W	D	E	F	G
Co(salen)	-(CH ₂) ₂ -	H	H	H	H
Co(3-MeOsalen)	-(CH ₂) ₂ -	CH ₃ O	H	H	H
Co(4,6-Me ₂ salen)	-(CH ₂) ₂ -	H	CH ₃	H	CH ₃
Co(Fsalen)	-(CH ₃) ₂ -	F	H	H	H

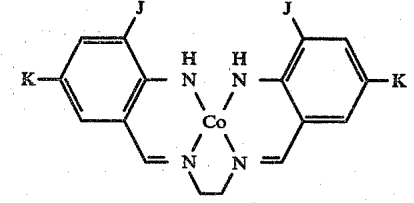
TABLE II-continued



Compound	W	D	E	F	G
Co(napsalen)	—(CH ₂) ₂ —	H	<i>b</i>	H	H
Co(saloph)	—C ₆ H ₄ —	H	H	H	H
Co(sal(±)or(m)bn)	$\begin{array}{c} \text{—CH—CH—} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	H	H	H	H
Co(sal(±)or(m)dpen)	$\begin{array}{c} \text{—CH—CH—} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	H	H	H	H
Co(sal(±)or(m)chxn)	$\begin{array}{c} \text{—CH—CH—} \\ \diagdown \quad / \\ (\text{CH}_2)_4 \end{array}$	H	H	H	H
Co(saldpt)	—(CH ₂) ₃ —NH—(CH ₂) ₃ —	H	H	H	H
Co(3-MeOsaldpt)	—(CH ₂) ₃ —NH—(CH ₂) ₃ —	CH ₃ O	H	H	H
Co(5-MeOsaldpt)	—(CH ₂) ₃ —NH—(CH ₂) ₃ —	H	H	CH ₃ O	H
Co(5-NO ₃ saldpt)	—(CH ₂) ₃ —NH—(CH ₂) ₃ —	H	H	NO ₂	H
Co(α-Mesaldpt)	—(CH ₂) ₃ —NH—(CH ₂) ₃ —	H	H	H	CH ₃
Co(salMedpt)	—(CH ₂) ₃ —NCH ₃ —(CH ₂) ₃ —	H	H	H	H
Co(3-MeOsalmMedpt)	—(CH ₂) ₃ —NCH ₃ —(CH ₂) ₃ —	CH ₃ O	H	H	H
Co(5-MeOsalmMedpt)	—(CH ₂) ₃ —NCH ₃ —(CH ₂) ₃ —	H	H	CH ₃ O	H
Co(α-MesalmMedpt)	—(CH ₂) ₃ —NCH ₃ —(CH ₂) ₃ —	H	H	H	CH ₃
Co(sal-n-Prdpt)	—(CH ₂) ₃ —N(n-C ₃ H ₇)—(CH ₂) ₃ —	H	H	H	H
Co(sal-i-Prdpt)	—(CH ₂) ₃ —N(i-C ₄ H ₉)—(CH ₂) ₃ —	H	H	H	H
Co(salBydpt)	—(CH ₂) ₃ —N(CH ₂ C ₆ H ₅)—	H	H	H	H
Co(salPhdpt)	—(CH ₂) ₃ —N(C ₆ H ₅)—(CH ₂) ₃ —	H	H	H	H
Co(sal-p-MeOPhdpt)	—(CH ₂) ₃ —N(p-CH ₃ OC ₆ H ₄)—	H	H	H	H
Co(5-BrsalMedapp)	—(CH ₂) ₃ —PCH ₃ —(CH ₂) ₃ —	H	H	Br	H
Co(3-MeosalMedapp)	—(CH ₂) ₃ —PCH ₃ —(CH ₂) ₃ —	CH ₃ O	H	H	H
Co(5-Brsaldape)	—(CH ₂) ₃ —O—(CH ₂) ₃ —	H	H	Br	H
Co(5-Claldape)	—(CH ₂) ₃ —O—(CH ₂) ₃ —	H	H	Cl	H
Co(saltmen)	$\begin{array}{c} \text{—C—C—} \\ \quad \\ (\text{CH}_3)_2 \quad (\text{CH}_3)_2 \end{array}$	H	H	H	H
Co(salpy)	—CH ₂ —CH(CH ₂ CH ₂ C ₃ H ₄ N)—	H	H	H	H

^bBenzene rings are replaced by naphthalene rings.

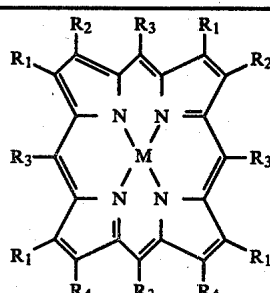
TABLE III



Compound	J	K
Co(amben)	H	H
Co(NO ₂ amben)	H	NO ₂
Co(MeOamben)	MeO	H
Co(cyen) ^c	H	H

^cethylene bridge replaces the two protons on the nitrogen atoms.

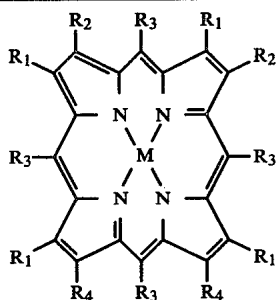
TABLE IV



	R ₁	R ₂	R ₃	R ₄
Porphyrin				
65 Protoporphyrin IX	Me	V	H	P
Mesoporphyrin IX	Me	Et	H	P
Deuteroporphyrin IX	Me	H	H	P
Pyrroprophyrin XV	Me	Et	H	P
meso-Tetraphenylporphin	H	H	Ph	H
Octaethylporphyrin	Et	Et	H	Et

11

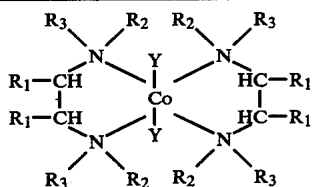
TABLE IV-continued



Porphyrin	R ₁	R ₂	R ₃	R ₄
2,4-Diacetyldeuteroporphyrin IX	Me	COCH ₃	H	P

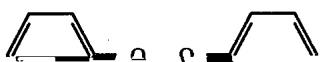
Abbreviations: Me, methyl; V, vinyl; P, propionic acid; Et, ethyl; Ph, phenyl.

TABLE V



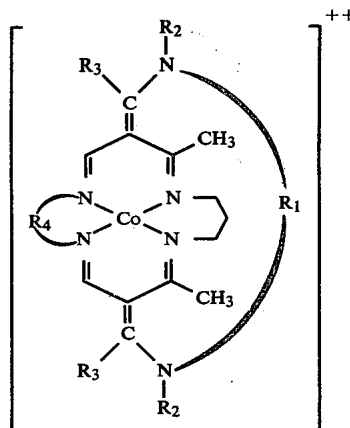
Compound	Y	R ₁	R ₂	R ₃
Co(s-Me ₂ en) ₂ Y ₂	Cl, Br, I, NO ₃ , SCN	H	CH ₃	H
Co(s-Me ₂ en) ₂ Y ₂	Cl, Br, I, NO ₃ , SCN	CH ₃	CH ₃	H
Co(s-Et ₂ en) ₂ Y ₂	Cl, Br, I, NO ₃ , SCN	H	C ₂ H ₅	H

Four of the most preferred carriers are N,N'-bis(-salicylideneimino)di-n-propylaminecobalt(II) [Co(-salPr)], N,N'-bis(3-methoxysalicylidene)ethylenediaminecobalt(II) [Co(3-MeOsalen)], N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II) [Co(3-MeOsaltmen)], and the Co(dry-caves), shown below:

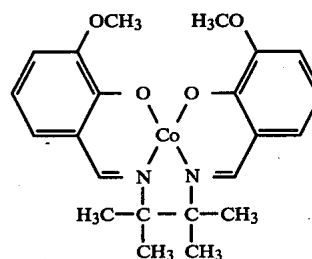


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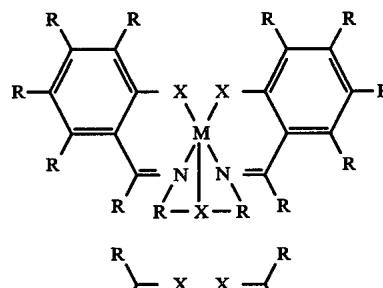
Co(dry-cave)*



Co(3-MeOsaltmen)

*Wherein R₁ is (CH₂)₄, (CH₂)₅, (CH₂)₆, (CH₂)₇, or (CH₂)₈ or branched-chain alkyl groups containing 4 to 8 carbon atoms; R₂ is CH₃ or H; R₃ is CH₃ or C₆H₅; R₄ is (CH₂)₂ or (CH₂)₃

When the configuration of the oxygen carrier is is



connected to a stripper section 4 which in turn is connected to a vacuum pump 5 for recovery of oxygen. Stripper section 4 may be provided with an outlet 6 for recycling oxygen-depleted solution to the absorber section 1. An oxygen analyzer (not shown) for determining the percentage of oxygen in the product stream, may be

Et₂en)₂(SCN)₂, Co[16](NMe)C₅-cave (a Co(dry cave) carrier) where R₁ is (CH₂)₅, R₂ and R₃ are CH₃, and R₄ is (CH₂)₃; Co[16](NMe)C₆-cave where R₁ is (CH₂)₆, R₂ is CH₃, R₃ is CH₃, and R₄ is (CH₂)₃; and Co(TpivPP) (a porphyrin) where R₁, R₂ and R₄ are hydrogen and R₃ is orthovalamidophenyl.

TABLE VI

Examples	Carrier Solution	Oxygen Absorption Pressure (mmHg)	Nitrogen Absorption Pressure (mmHg)	Oxygen Absorbed ($\frac{\text{cm}^3 \text{ (STP)}}{\text{liter}}$)	Nitrogen Absorbed ($\frac{\text{cm}^3 \text{ (STP)}}{\text{liter}}$)	Maximum Oxygen Content of Product Gas (%)
1	0.05M Co(salPr) in DMSO	160	500	390	22	95
2	0.2M Co(3-MeOsaltmen) + 0.6M DMAP + 0.55M H ₂ O in NMP*	140	540	1320	32	97
3	0.075M Co(s-Et ₂ en)(NO ₃) ₂ + 2M s-Et ₂ en** in formamide	22	82	277	3.5	98.8
4	0.15M Co(s-Et ₂ en) ₂ (SCN) ₂ + 0.7M s-Et ₂ en in formamide	160	600	>260	14	>95
5	0.01M Co[16](NMe)C ₅ -cave + 0.5M 1-MeIm in BLO	130	480	140	26	84
6	0.01M Co[16](NMe)C ₆ -cave + 1.5M 1-MeIm in DMSO	30	110	200	4	98
7	0.01M Co[16](NMe)C ₆ -cave + 1.5M 1-MeIm in DMSO	120	450	240	17	93
8	0.005M Co(TpivPP) + 0.01 1-MeIm in TBP	110	410	90	47	66

* -5° C.

**s-Et₂en does not act as an axial base, but rather promotes the formation of a form of Co(s-Et₂en)₂(NO₃)₂ that is active toward oxygen.

utilized either before or after the vacuum pump 5. The outlet of the vacuum pump 5 may be connected to a storage or surge tank (not shown) for storage of the recovered oxygen. Nitrogen-enriched air may be taken off through another outlet 3 of stripper section 1 by suitable means such as a fan 7. If desired, a flow meter or regulator (not shown) may also be used at either of the product-stream outlets.

EXAMPLES

Absorption of oxygen and nitrogen by carrier solutions was demonstrated using a calibrated vacuum apparatus to control the temperature, pressure and volume of the gases and solutions. To measure the oxygen or nitrogen sorption of a carrier solution, a known volume of the solution was placed in a small, stirred vial. The vial was then evacuated to degas the solution. A known volume of gas was then introduced into the vial from a gas burette, and the gas absorbed by the solution was calculated from measurement of the pressure and volume of the remaining gas. Different oxygen absorption pressures were tested in these examples; however, the nitrogen absorption pressure tested was always 3.7 times higher than the oxygen pressure, which is the ratio of partial pressures in air. The oxygen content of the product gas was calculated from the measured amounts of oxygen and nitrogen absorbed. In all cases except Example 2, the absorbed oxygen was desorbed from the carrier solution by decreasing the partial pressure of oxygen by completely evacuating the vial. In some cases, the absorption/desorption cycle was repeated to verify the stability of the process.

Representative results of oxygen and nitrogen absorption tests at 25° C. with carrier solutions are presented in Table VI. The oxygen carriers used in these examples were Co(salPr), Co(3-MeOsaltmen), Co(s-

DMAP), N-N'-diethylethylenediamine (s-Et₂en), and 1-methylimidazole (1-MeIm), and solvents were dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP), formamide, and gamma-butyrolactone (BLO). In these tests, the oxygen and nitrogen absorption and desorption were measured and the maximum oxygen content of the product gas was calculated assuming complete removal of oxygen and nitrogen from the carrier solution in the desorption mode. The highest oxygen content of gas produced in these examples was 98.8%, which approaches that produced by cryogenic fractionation, and which is much higher than that produced by PSA processes. Several of these carrier solutions produced gas of greater than 95% oxygen content, and one (Example 4) was subjected to three absorption/desorption cycles with no loss in performance.

The carrier solution of Example 2 was subjected to four absorption/desorption cycles in which desorption was accomplished by raising the temperature from -5° C. to 25° C. rather than by decreasing the pressure as in the other examples. No loss in performance was observed. Considerable improvement in the performance shown in the examples is to be expected by using more concentrated carrier solutions in combination with solvents that have lower nitrogen solubilities. It should be noted that identical carrier solutions, when used in membrane configurations, maintain satisfactory oxygen-carrying performance for at least about 100 days, which in a diffusion-controlled process corresponds to at least about 400,000 absorption/desorption cycles. Excellent performance stability is therefore to be expected with the absorption process.

The terms and expressions which have been employed in the foregoing specification are used therein as

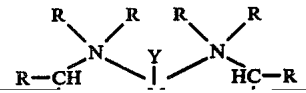
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terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding equivalents of the features shown and described or portions thereof, it being recognized that the scope of the invention is defined and limited only by the

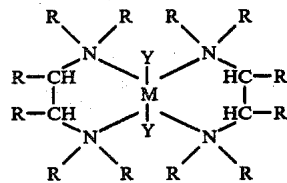
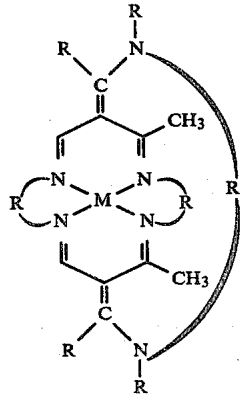
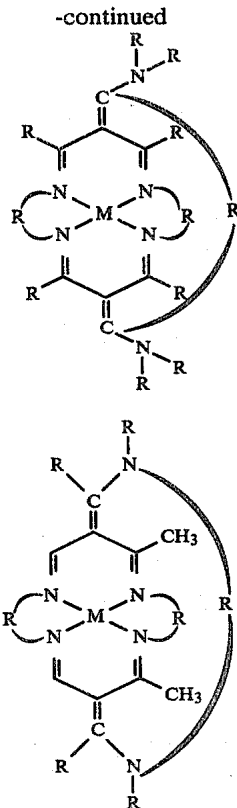
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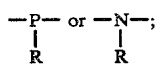
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wherein

M is a metal selected from cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,



R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety; and

Y is halide, nitrate, thiocyanate or cyanide; said solution absorbing oxygen from said gaseous oxygen-containing feed stream;

(b) desorbing oxygen from said solution to a gaseous product stream; and

(c) collecting oxygen from the product stream after the oxygen has been desorbed.

3. The process of claims 1 or 2 wherein said desorption of oxygen is accomplished by bringing said solution into contact with a gaseous product stream with an oxygen partial pressure substantially less than that of said feed stream.

4. The process of claims 1 or 2 wherein said desorption of oxygen is accomplished by heating said solution and bringing it into contact with said gaseous product stream.

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5. The process of claims 4 wherein the temperature of the feed stream is between about -50°C . and $+95^{\circ}\text{C}$. and the temperature of the product stream is at least about 5°C . higher than the temperature of the feed stream.

6. The process of claim 1 or 2 wherein the metal is cobalt.

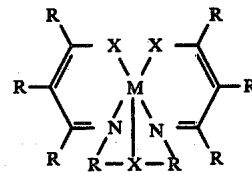
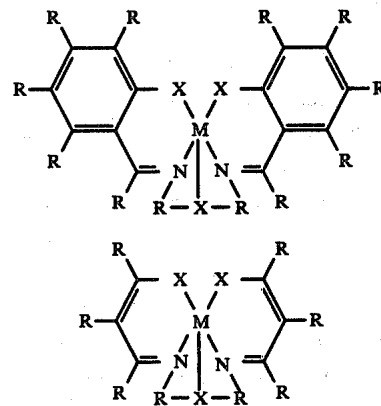
7. The process of claims 3 wherein the oxygen partial pressure of the product stream is at least about 10 mmHg less than the oxygen partial pressure of the feed stream.

8. The process of claim 7 wherein the oxygen partial pressure of the feed stream is substantially atmospheric or less than atmospheric.

9. The process of claim 7 wherein the oxygen partial pressure of the feed stream is at least about 10 mmHg higher than atmospheric and the oxygen partial pressure of the product stream is substantially atmospheric.

10. A process for the separation and purification of oxygen and nitrogen comprising:

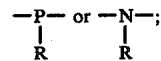
(a) bringing an atmospheric air feed stream into contact with a solution containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture being capable of dissolving said pentacoordinate oxygen carrier, and said pentacoordinate oxygen carrier being a metal-containing complex having any of the structures



wherein

M is a metal selected from cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,



and

R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety; said solution absorbing oxygen from said atmospheric air feed stream;

(b) collecting nitrogen from the atmospheric air feed stream after the oxygen has been absorbed;

(c) desorbing oxygen from said solution to a gaseous product stream; and

(d) collecting oxygen from the product stream after the oxygen has been desorbed.

11. The process of claims 1, 2, or 10 wherein the rates of absorption of oxygen into or desorption of oxygen

from said solution are increased either by stirring or otherwise agitating said solution or by increasing the interfacial area between said feed stream and said solution, said interfacial area being increased by any of the following methods:

- (a) bubbling said feed stream through said solution;
- (b) spraying said solution through said feed stream;
- (c) forming a foam of said solution with said feed stream;
- (d) incorporating said solution into microporous beads; or
- (e) contacting said solution with said feed stream in a sieve-tray column or packed column.

12. The process of claims 1, 2 or 10 conducted at a temperature of between about -50°C . and $+100^{\circ}\text{C}$.

13. The process of claims 1, 2 or 10 wherein the solvent is selected from lactones, lactams, sulfoxides, nitriles, amides, amines, esters, ethers, other nitrogen-containing liquids, water and mixtures thereof,

the axial base is selected from secondary or tertiary nitrogen-atom-containing Lewis bases, imidazoles, ketones, amides, amines, sulfoxides and pyridines, and

the oxygen carrier is selected from metal-containing bis(acetylacetonate)ethylenediimines, $\text{N,N}'$ -bis(salicylidene)ethylenediamines, bis(2-amino-1-benzaldehyde)ethylenediimines, dry-cave compounds, and $\text{N,N}'$ -substituted-ethylenediamines.

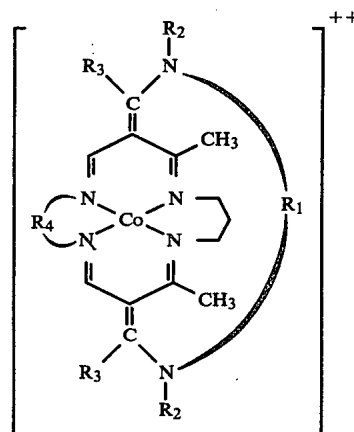
14. The process of claim 13 wherein the solvent is selected from at least one of gamma-butyrolactone, dimethylsulfoxide, propylene carbonate, diethylsulfoxide, N -methylpyrrolidone, dimethylacetamide, dimethylformamide, formamide, gamma-valerolactone, delta-valerolactone, epsilon-caprolactone, tributylphosphate, diglyme and benzonitrile, and

the axial base is selected from at least one of 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, dimethylsulfoxide, $\text{N,N}'$ -diethylethylenediamine, 4-dimethylaminopyridine, 4-aminopyridine, 4,4-bipyridine, 4-methoxypyridine, 4-methylaminopyridine, 3,4-lutidine, 3,5-lutidine, pyridine, 4-methylpyridine, 4-cyanopyridine, pyrazine, 4-pyrrolidinopyridine and piperidine.

15. The process of claim 14 wherein the oxygen carrier is $\text{N,N}'$ -bis(3-methoxysalicylidene)ethylenediaminecobalt(II).

16. The process of claim 14 wherein the oxygen carrier is $\text{N,N}'$ -bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

17. The process of claim 14 wherein the oxygen carrier is



wherein

R_1 is a branched or straight-chain hydrocarbon or hetero-atom-containing bridge;

R_2 is hydrogen or methyl;

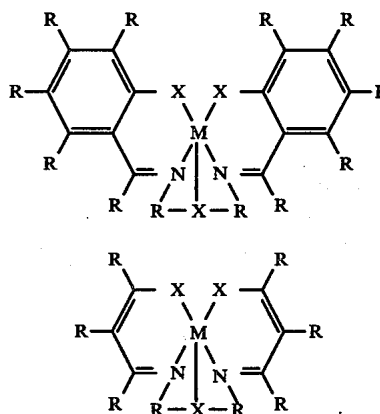
R_3 is methyl or benzyl; and

R_4 is alkyl containing 2 to 3-carbon atoms.

18. The process of claims 1 or 10 wherein desorption is performed in two stages, the first of which results in desorption of a small percentage of the absorbed oxygen and a large percentage of the absorbed nitrogen, and the second stage of which results in desorption of a large percentage of the absorbed oxygen and a small percentage of the absorbed nitrogen.

19. A process for the separation and purification of oxygen comprising:

- (a) bringing a gaseous, oxygen-containing feed stream into contact with a solution containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture being capable of dissolving said pentacoordinate oxygen carrier, and said pentacoordinate oxygen carrier being a metal-containing complex having any of the structures

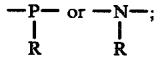


wherein

M is a metal selected from cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is $-\text{O}-$, $-\text{S}-$,

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and

R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety;

said solution absorbing oxygen from said atmospheric air feed stream;

(b) desorbing oxygen from said solution to a gaseous product stream; and

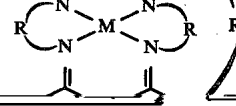
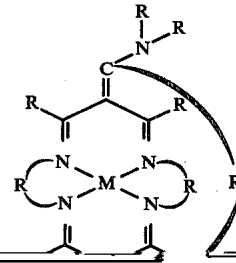
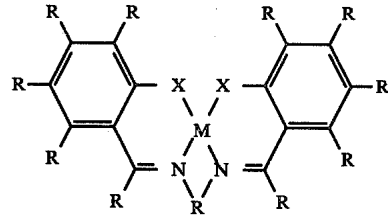
(c) collecting oxygen from the product stream after the oxygen has been desorbed.

20. The process of claims 10 or 19 wherein said description of oxygen is accomplished by bringing said solution into contact with a gaseous product stream with an oxygen partial pressure substantially less than that of said feed stream.

21. The process of claims 10 or 19 wherein said de-

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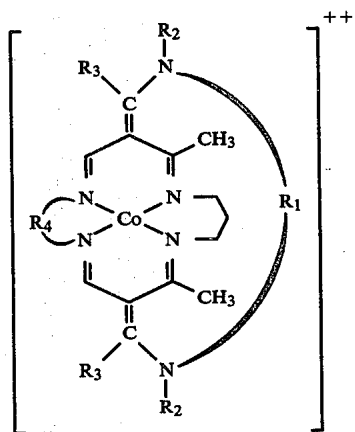
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tertiary nitrogen atoms, imidazoles, ketones, amides, amines, sulfoxides, pyrazines and pyridines.

30. The solution of claim 29 wherein the solvent is selected from lactones, lactams, sulfoxides, nitriles, amides, amines, esters, ethers, other nitrogen-containing liquids, water and mixtures thereof,

the axial base is selected from at least one of 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, dimethylsulfoxide, N,N'-diethylethylenediamine, 4-dimethylaminopyridine, 4-aminopyridine, 4,4-bipyridine, 4-methoxypyridine, 4-methylaminopyridine, 3,4-lutidine, 3,5-lutidine, pyridine, 4-methylpyridine, 4-cyanopyridine, piperidine, 4-pyrrolidinopyridine and pyrazine, and the oxygen carrier is selected from N,N'-bis(3-methoxysalicylidene)ethylenediaminecobalt(II), N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II), and



wherein

R₁ is a branched or straight-chain hydrocarbon or hetero-atom-containing bridge;

R₂ is hydrogen or methyl;

R₃ is methyl or benzyl; and

R₄ is alkyl containing 2 to 3 carbon atoms.

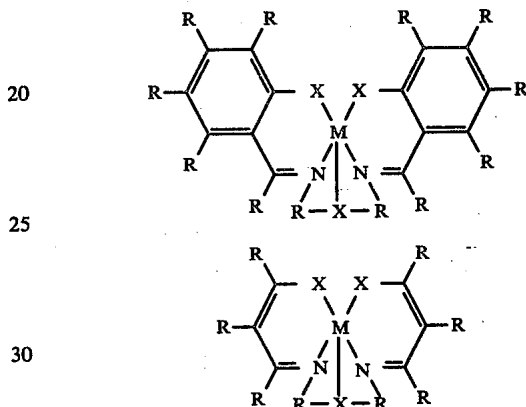
31. The solution of claim 29 wherein the solvent is selected from gamma-butyrolactone and N-methylpyrrolidone or mixtures thereof, the axial base is 4-dimethylaminopyridine and the oxygen carrier is N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

32. The solution of claim 29 wherein the solvent is selected from gamma-butyrolactone and N-methylpyr-

rolidone or mixtures thereof, the axial base is selected from 4-aminopyridine and 4-cyanopyridine and the oxygen carrier is N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

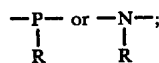
33. The solution of claims 30, 31 or 32 wherein the solvent contains an additive of less than 20 wt%, the additive being selected from the group consisting of water, organic or inorganic acids or bases.

34. A solution useful for the separation of oxygen and nitrogen from atmospheric air comprising a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture being capable of dissolving said pentacoordinate oxygen carrier, and said pentacoordinate oxygen carrier being a metal-containing complex having any of the structures



wherein

M is a metal selected from cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;
X is —O—, —S—,



and

R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety.

35. The solution of claim 34 wherein the metal is cobalt and the solvent is selected from lactones, lactams, sulfoxides, nitriles, amides, amines, nitrogen-containing liquids, esters, ethers, water and mixtures thereof.

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