United States Patent [19]

Roman et al.

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[45] **Date of Patent: Sep. 17, 1985**

[54] **METHOD AND APPARATUS FOR PRODUCING OXYGEN AND NITROGEN AND MEMBRANE THEREFOR**

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[73] Assignee: **Bend Research, Inc.**, Bend, Oreg.

[21] Appl. No.: **393,712**

[22] Filed: **Jun. 30, 1982**

[51] **Int. Cl.**[4] **C01B 13/02**

[52] **U.S. Cl.** **423/579**; 55/16; 55/68; 55/158; 422/122; 422/177; 422/211; 423/219; 436/178

[58] **Field of Search** 55/16, 158, 68; 423/579, 219; 422/122, 177, 211; 436/178

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,388,095	10/1945	Stahly	55/16
2,824,620	2/1958	De Rosset	55/16
2,892,508	6/1959	Kohman et al.	55/16

J. Am. Chem. Soc., 101, 1622, (1979).
J. Am. Chem. Soc., 102, 3283, (1980).
European Patent Office, How to Get a European Patent–Guide for Applicants, paragraph 77.

Primary Examiner—John Doll
Assistant Examiner—Wayne A. Lange
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[57] **ABSTRACT**

Process and apparatus for the separation and purification of oxygen and nitrogen as well as a novel membrane useful therein are disclosed. The process utilizes novel facilitated transport membranes to selectively transport oxygen from one gaseous stream to another, leaving nitrogen as a byproduct. In the method, an oxygen carrier capable of reversibly binding molecular oxygen is dissolved in a polar organic membrane which separates a gaseous feed stream such as atmospheric air and a gaseous product stream. The feed stream is maintained at a sufficiently high oxygen pressure to keep the oxygen carrier in its oxygenated form at the interface of the feed stream with the membrane, while the product-

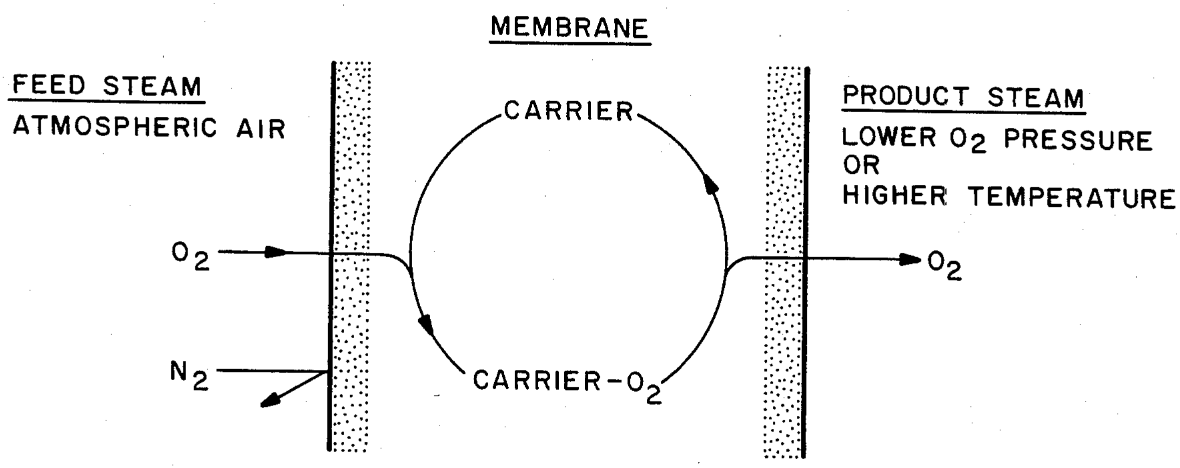

MEMBRANE
FEED STEAM
ATMOSPHERIC AIR
CARRIER
PRODUCT STEAM
LOWER O2 PRESSURE
OR
HIGHER TEMPERATURE
O2
O2
N2
CARRIER-O2

FIG. 1

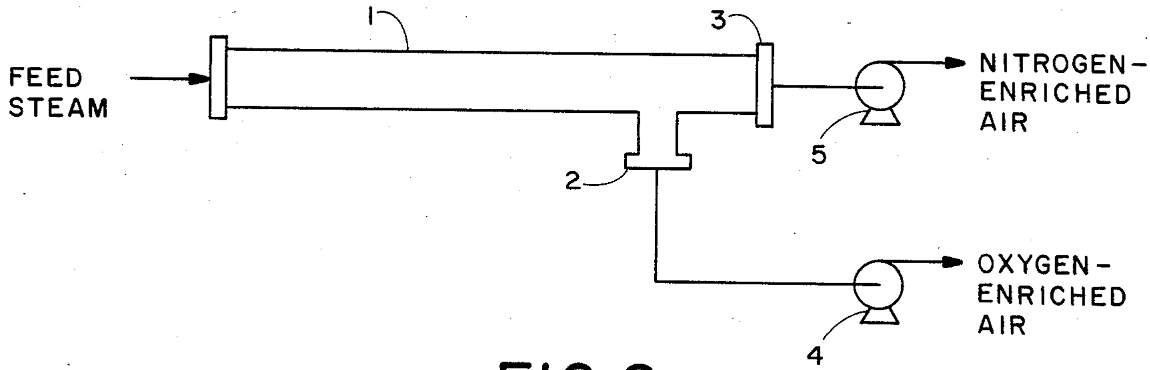

1
3
FEED
STEAM
NITROGEN-
ENRICHED
AIR
5
2
OXYGEN-
ENRICHED
AIR
4

FIG. 2

METHOD AND APPARATUS FOR PRODUCING OXYGEN AND NITROGEN AND MEMBRANE THEREFOR

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

It was observed by Tsumaki over forty years ago in *Bull. Chem. Soc. Japan* 13 (1938) 252 that synthetic chelate-type compounds reversibly bind oxygen. However, attempts to formulate a commercially feasible process for the production of oxygen- and nitrogen-enriched air using a membrane process have been unsuccessful to date.

The first demonstration of facilitated transport of of the membrane at least about 5° C. higher than that of the feed stream.

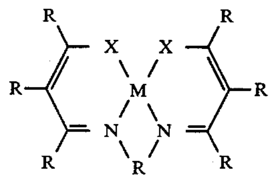
In the process of the present invention, it has been discovered that certain combinations of solvents and nitrogen- and/or oxygen-containing Lewis bases defined as "axial bases" unexpectedly enhance the ability of certain metal-containing complexes to selectively and rapidly transport oxygen across membranes to a degree never before thought possible in the art, while at the same time allowing extended life of the liquid membrane carrier system beyond anything encountered or [illegible] in the prior art. Oxygen to nitrogen selectivi-

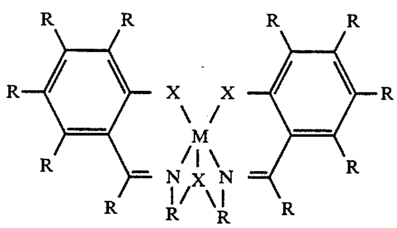
pressures on the feed side of the membrane are also acceptable so long as the partial pressure of oxygen on the product side 2 of the membrane is at least approximately 10 mmHg lower than the oxygen partial pressure on the feed side, or the temperature on the product side of the membrane is at least approximately 5° C. higher than the temperature on the feed side of the membrane. The feed stream input may be controlled by a flow meter or regulator (not shown) on the feed stream side of the membrane module 1. The lower partial pressure on the product side may be maintained by any suitable means, for example a vacuum pump 4

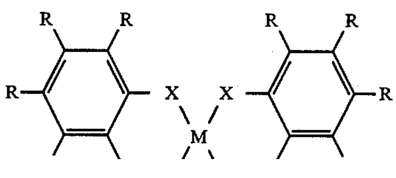
Classes of useful solvents include lactones, lactams, sulfoxides, nitriles, amides, amines, esters, ethers and other nitrogen-containing liquids. Preferred examples include gamma-butyrolactone, dimethylsulfoxide, N-methylpyrrolidone, propylene carbonate, dimethylacetamide, gamma-valerolactone, delta-valerolactone, epsilon-caprolactone, diethylsulfoxide, benzonitrile, and tributylphosphate. In addition, oligomers or polymers of these classes of solvents may be useful.

Generally speaking, "axial bases," or certain classes of Lewis bases usually containing a nitrogen atom or in some cases an oxygen, or sulfur, or phosphorus atom, or a combination of these must be present in the novel [illegible] 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, 4-pyrrolidinopyridine, 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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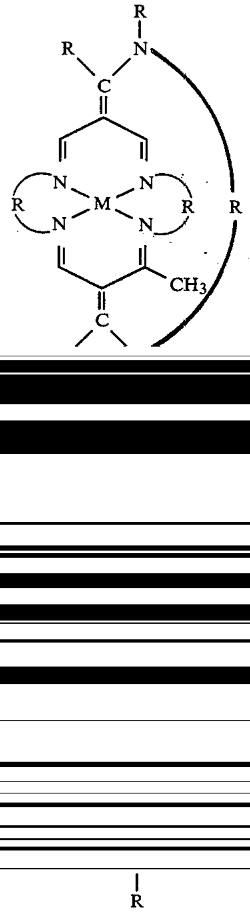
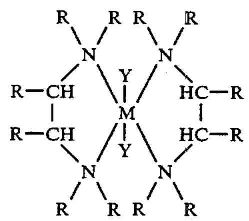
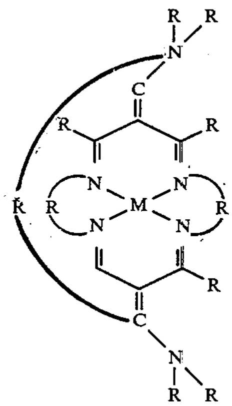


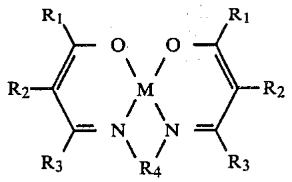




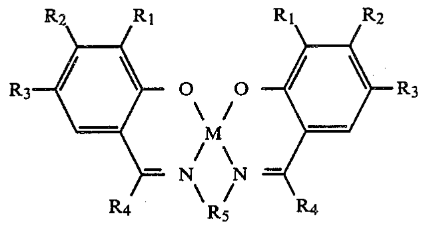
wherein M represents a metal such as cobalt, iron, nickel, copper, manganese, ruthenium, or rhodium; X is —O—, —S—,

$$-\underset{R}{\underset{|}{P}}-, \text{ or } -\underset{R}{\underset{|}{N}}-;$$

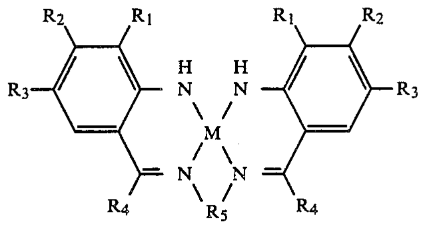
R is hydrogen, alkyl, aryl, halogen, alkoxy, or a nitrogen-containing moiety; and Y represents a halide, nitrate, thiocyanate, or cyanide anion. Preferred metals are cobalt(II) and iron(II). Successful carriers must



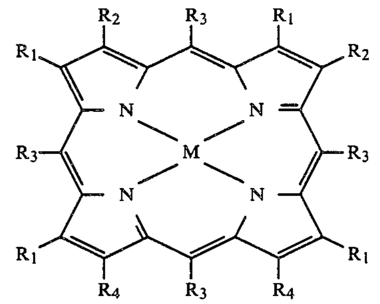
Bis(acetylacetone) ethylenediimine derivatives



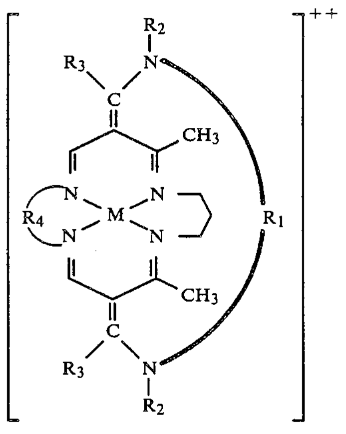
N,N'—bis(salicylidene)ethylenediamine derivatives



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



Porphyrin derivatives



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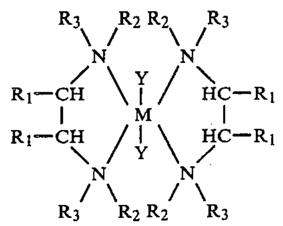
"Dry-cave" complex derivatives

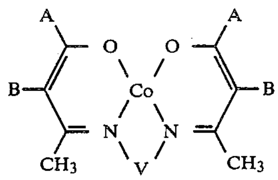


N,N'—substituted ethylenediimine derivatives

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.

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.

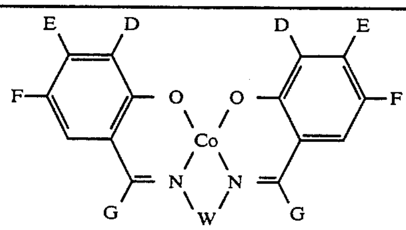
TABLE I



Compound	V	A	B
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_6H_5
Co(benacen)	$-(CH_2)_2-$	C_6H_5	H
Co(Clbenacen)	$-(CH_2)_2-$	p-ClC_6H_4	H
Co(Brbenacen)	$-(CH_2)_2-$	p-BrC_6H_4	H
Co(Mebenacen)	$-(CH_2)_2-$	p-$CH_3C_6H_4$	H
Co(Meobenacen)	$-(CH_2)_2-$	p-$CH_3OC_6H_4$	H
Co(bensacen)[a]	$-(CH_2)_2-$	C_6H_5	H
Co(Clbensacen)[a]	$-(CH_2)_2-$	p-ClC_6H_4	H
Co(Brbensacen)[a]	$-(CH_2)_2-$	p-BrC_6H_4	H
Co(Mebensacen)[a]	$-(CH_2)_2-$	p-$CH_3C_6H_4$	H
Co(Meobensacen)[a]	$-(CH_2)_2-$	p-$CH_3OC_6H_4$	H
Co(sacacen)[a]	$-(CH_2)_2-$	CH_3	H
Co(sacacen)[a]	$-(CH_2)_2-$	CH_3	H
Co(sacsacpn)[a]	$-CH_2-CH(CH_3)-$	CH_3	H
Co(sacsactn)	$-(CH_2)_3-$	CH_3	H
Co(sacsacchxn)	$-CH_2-CH_2-$ $(CH_2)_4$	CH_3	H

[a] oxygen atoms are replaced by sulfur

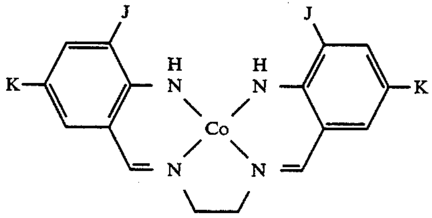
TABLE II



Compound	W	D	E	F	G
Co(salen)	—$(CH_2)_2$—	H	H	H	H
Co(3-MeOsalen)	—$(CH_2)_2$—	CH_3O	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
Co(napsalen)	—$(CH_2)_2$—	H	b	H	H
Co(saloph)	—C_6H_4—	H	H	H	H
Co(sal(±) or (m)bn)	—CH(CH$_3$)—CH(CH$_3$)—	H	H	H	H
Co(sal(±) or (m)dpen)	—CH(C$_6$H$_5$)—CH(C$_6$H$_5$)—	H	H	H	H
Co(sal(±) or (m)chxn)	—CH—CH— bridged by $(CH_2)_4$	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_3O	H	H	H
Co(5-MeOsaldpt)	—$(CH_2)_3$—NH—$(CH_2)_3$—	H	H	CH_3O	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-MeOsalMedpt)	—$(CH_2)_3$—NCH_3—$(CH_2)_3$—	CH_3O	H	H	H
Co(5-MeOsalMedpt)	—$(CH_2)_3$—NCH_3—$(CH_2)_3$—	H	H	CH_3O	H
Co(α-MesalMedpt)	—$(CH_2)_3$—NCH_3—$(CH_2)_3$—	H	H	H	CH_3
Co(sal-n-Prdpt)	—$(CH_2)_3$—N(n-C_3H_2)—$(CH_2)_3$—	H	H	H	H
Co(sal-i-Prdpt)	—$(CH_2)_3$—N(i-C_4H_9)—$(CH_2)_3$—	H	H	H	H
Co(salBydpt)	—$(CH_2)_3$—N($CH_2C_6H_5$)—$(CH_2)_3$—	H	H	H	H
Co(salPhdpt)	—$(CH_2)_3$—N(C_6H_5)—$(CH_2)_3$—	H	H	H	H
Co(sal-p-MeOPhdpt	—$(CH_2)_3$—N(p-$CH_3OC_6H_4$)—$(CH_2)_3$—	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_3O	H	H	H
Co(5-Brsaldape)	—$(CH_2)_3$—O—$(CH_2)_3$—	H	H	Br	H
Co(5-Clsaldape)	—$(CH_2)_3$—O—$(CH_2)_3$—	H	H	Cl	H
Co(saltmen)	—C(CH_3)$_2$—C(CH_3)$_2$—	H	H	H	H
Co(salpy)	—CH_2—CH($CH_2CH_2C_5H_4N$)—	H	H	H	H

[b]Benzene rings are replaced by naphthalene rings.

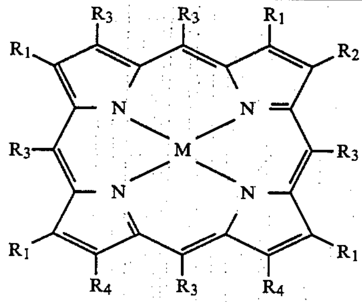
TABLE III



Compound	J	K
Co(amben)	H	H
Co(NO$_2$amben)	H	NO_2
Co(MeOamben)	MeO	H
Co(cyen)[c]	H	H

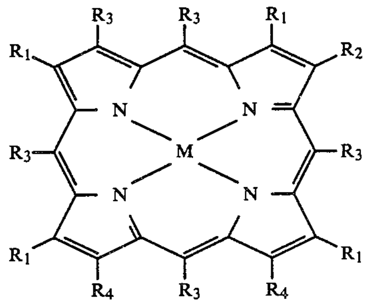
[c]ethylene bridge replaces the two protons on the nitrogen atoms.

TABLE IV



Porphyrin	R_1	R_2	R_3	R_4
Protoporphyrin IX	Me	V	H	P
Mesoporphyrin IX	Me	Et	H	P
Deuteroporphyrin IX	Me	H	H	P
Pyrroporphyrin XV	Me	Et	H	P

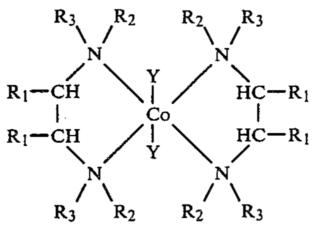
TABLE IV-continued



Porphyrin	R_1	R_2	R_3	R_4
meso-Tetraphenylporphin	H	H	Ph	H
Octaethylporphyrin	Et	Et	H	Et
2,4-Diacetyldeutero-porphyrin IX	Me	$COCH_3$	H	P

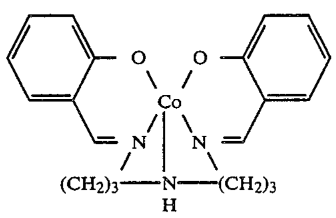
Abbreviations: Me, methyl; V, vinyl; P, propionic acid; Et, ethyl; Ph, phenyl.

TABLE V

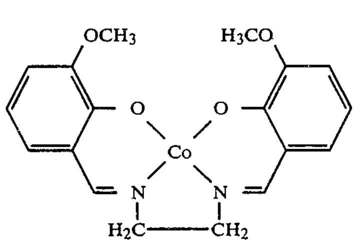


Compound	Y	R_1	R_2	R_3
$Co(s\text{-}Me_2en)_2Y_2$	Cl, Br, I, NO_3, SCN	H	CH_3	H
$Co(s\text{-}Me_2en)_2Y_2$	Cl, Br, I, NO_3, SCN	CH_3	CH_3	H
$Co(s\text{-}Et_2en)_2Y_2$	Cl, Br, I, NO_3, SCN	H	C_2H_5	H

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



Co(salPr)



Co(3-MeOsalen)

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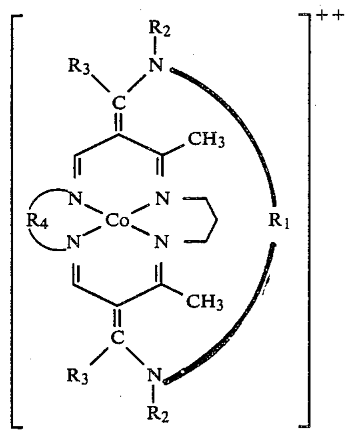
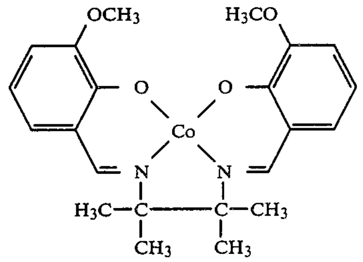


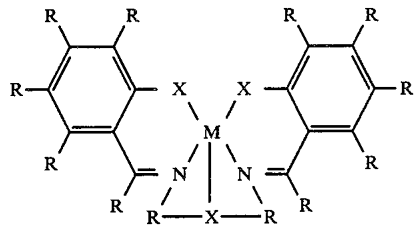
Co(dry-cave)*

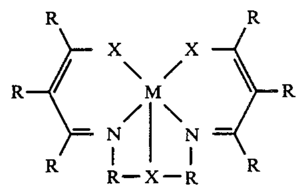


Co(3-MeOsaltmen)

*Wherein R_1 is $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_7$, or $(CH_2)_8$ or branched-chain alkyl groups containing 4 to 8 carbon atoms; R_2 is CH_3 or H; R_3 is CH_3 or C_6H_5; R_4 is $(CH_2)_2$

When the configuration of the oxygen carrier is is





the axial base may be dispensed with, for the reason that there are sufficient oxygen, nitrogen, or sulfur coordinating atoms present within the carrier itself.

In the case of Co(3-MeOsaltmen) and perhaps in other cases, small amounts of added water (on the order of less than 20% by volume) enhance carrier performance. This is unexpected in view of the fact that protic solvents such as water are generally known to irreversibly oxidize such metal complexes. A similar effect predictably occurs with some inorganic or organic acids, bases, or alcohols.

The membrane module 1 is preferably provided with one or more product-stream apertures 2 and 3 for the recovery of product. As shown in FIG. 2, aperture 2 is connected to a vacuum pump 4 for recovery of oxygen.

An oxygen analyzer (not shown) for determining the percentage of oxygen in the product stream, may be utilized either before or after the vacuum pump 4. The outlet of the vacuum pump 4 may be connected to a storage or surge tank (not shown) for storage of the recovered oxygen. The oxygen-depleted or nitrogen-enriched air is taken off through another aperture 3 of module 1 by suitable means such as a fan 5. If desired, a flow meter or regulator (not shown) may also be used at either of the product-stream apertures.

EXAMPLES

Facilitated-transport membranes of the present invention were prepared by immersing a microporous polymeric film in a liquid comprising the oxygen carrier, axial base, and solvent. In the examples given below, the microporous membrane support was 130-μm-thick nylon 6,6, commercially available as Ultipor® NM, made by Pall Trinity Micro Corporation of Cortland, N.Y. The pores of the film became filled with the liquid by capillary action. The loaded membrane was then placed between the two compartments of a permeation cell and was degassed prior to the permeation measurement. The feed-side oxygen partial pressure was maintained at 160 mmHg. The product-side oxygen partial pressure was then adjusted as indicated, and the gas flux was determined by measuring the velocity of a mercury droplet in a calibrated capillary flow meter. The measured flux was normalized for membrane thickness and porosity to yield the permeability. In some cases the oxygen concentration in the product stream was measured by gas chromatography. The remainder of the conditions were as noted in the tables that follow.

Representative results of tests at 25° C. showing facilitated transport of oxygen with atmospheric air as the feed and the Co(dry-cave) oxygen carriers are presented in Table VI. The oxygen carriers used in these examples are located as Co[16](NMe)C_6-cave where R_1 is $(CH_2)_6$, R_2 and R_3 *are* CH_3, and R_4 is $(CH_2)_3$; and Co[16](NMe)C_5-cave where R_1 is $(CH_2)_5$, R_2 is CH_3, R_3 is CH_3, and R_4 is $(CH_2)_3$. The axial base used was 1-methylimidazole (1-MeIm) and the solvent was dimethylsulfoxide (DMSO). The highest oxygen permeability recorded was greater than that of silicone rubber, which is the most oxygen-permeable polymeric membrane known. The highest selectivity was 25, which is

TABLE VI

Membrane	Product-Side Pressure (mmHg)	Oxygen Permeability $\left(\frac{10^{-9}\ cm^3\text{-}cm}{cm^2\text{-}sec\text{-}cmHg}\right)$	O_2/N_2 Selectivity	Oxygen Content of Product Gas (%)
0.02 M Co[16](NMe)C_6-cave + 1.5 M 1-MeIm in DMSO	1	28	8.7	69
	10	17	5.4	58
0.10 M Co[16](NMe) C_6-cave + 1.5 M 1-MeIm in DMSO	1	61	20	84
	10	33	10	70
0.02 M Co[16](NMe)C_5-cave + 1.5 M 1-MeIm in DMSO	1	22	7.3	66
	10	21	7.0	61
0.20 M Co[16](NMe)C_5-cave + 0.5 M 1-MeIm in DMSO	1	75	25	87

Facilitated transport of oxygen with Co(salPr), Co(3-MeOsalen), and Co(3-MeOsaltmen) is shown in Table VII. Co(salPr) did not require an axial base, and 4-dimethylaminopyridine (DMAP) was used as the axial base with the other carriers. Solvents used in these examples included DMSO, gamma-butyrolactone, dimethylacetamide (DMAC), and N-methylpyrrolidone (NMP). The highest oxygen permeability recorded was more than twice that of silicone rubber, and the highest oxygen-to-nitrogen selectivity was 30, which resulted in the production of 88% oxygen from air in a single pass through the membrane. Liquid membranes of the type shown in Table VII proved to be exceptionally and unexpectedly stable, producing approximately 65 to 80% oxygen from air for longer than 3 months.

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

TABLE VII

Product-Side Pressure	Temperature	Oxygen Permeability $\left(\frac{10^{-9}\ cm^3\text{-}cm}{\ }\right)$	O_2/N_2	Oxygen Content of Product

TABLE VII-continued

Membrane	Product-Side Pressure (mmHg)	Temperature (°C.)	Oxygen Permeability $\left(\frac{10^{-9}\ cm^3\text{-}cm}{cm^2\text{-}sec\text{-}cmHg}\right)$	O_2/N_2 Selectivity	Oxygen Content of Product Gas (%)
DMSO and ν-butyrolactone 0.4 M Co(3MeIsaltmen) + 0.6 M DMAP + 0.5 M H_2O in NMP	25	−10	60*	16	79

*Calculated from measured oxygen content of permeating gas.

What is claimed is:

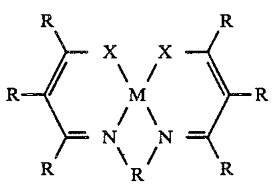
1. A process for the separation and purification of oxygen and nitrogen comprising:

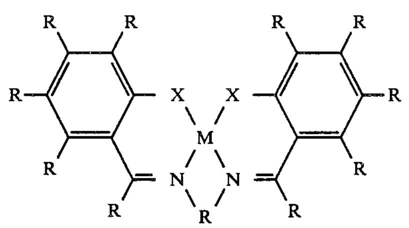
(a) bringing atmospheric air into contact with a membrane, said membrane separating said atmospheric air into a feed stream on one side of said membrane and a product stream on the other side of said membrane,

(b) maintaining the oxygen partial pressure on the product-stream side of said membrane at least approximately 10 mmHg lower than the oxygen partial pressure on the feed-stream side of said membrane,

(c) collecting oxygen from the product-stream side of said membrane and nitrogen from the feed-stream side of said membrane,

(d) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture, an axial base, and an oxygen carrier, said solvent or solvent mixture, axial base and oxygen carrier being in the liquid phase when present together, said solvent or solvent mixture being capable of dissolving the axial base and the oxygen carrier when they are present together, said axial base being capable of providing a coordinating atom to the oxygen carrier, and said oxygen carrier being a metal-containing complex having any of the structures





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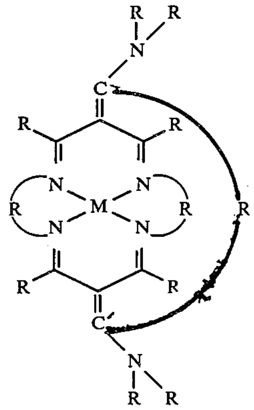

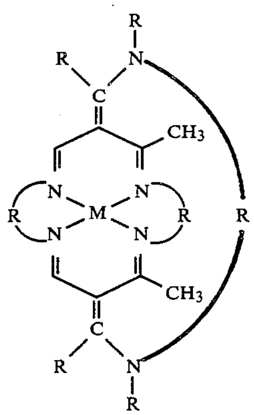

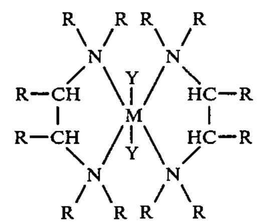

wherein

M is cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

—P(R)— or —N(R)—;

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

Y is halide, nitrate, thiocyanate or cyanide.

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

(a) bringing a gaseous oxygen-containing stream into contact with a membrane, said membrane separating said gaseous oxygen-containing stream into a feed stream on one side of said membrane and a product stream on the other side of said membrane,

(b) maintaining the oxygen partial pressure on the

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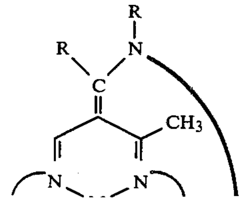
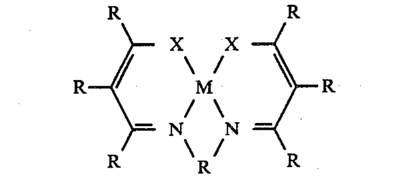
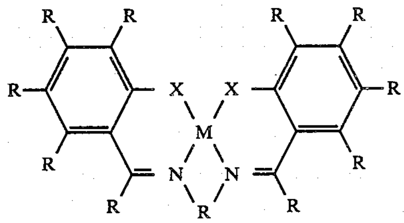
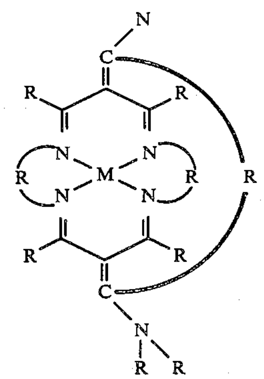
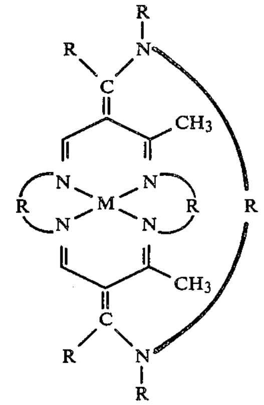


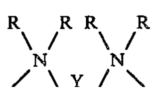
atom to the oxygen carrier, and said oxygen carrier being a metal-containing complex having any of the structures

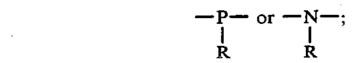












R is hydrogen, alkyl, aryl, halogen, alkoxy or a nitrogen-containing moiety; and

Y is halide, nitrate, thiocyanate or cyanide.

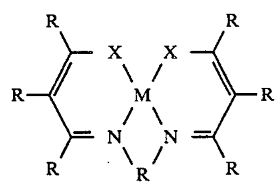
4. A process for the separation and purification of oxygen comprising:

(a) bringing a gaseous oxygen-containing stream into contact with a membrane, said membrane separating said gaseous oxygen-containing stream into a feed stream on one side of said membrane and a product stream on the other side of said membrane,

(b) maintaining the temperature on the product-stream side of said membrane at least approximately 5° C. higher than the temperature on the [illegible]

(c) collecting oxygen from the product-stream side of said membrane,

(d) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture, an axial base and an oxygen carrier, said solvent or solvent mixture, axial base and oxygen carrier being in the liquid phase when present together, said solvent or solvent mixture being capable of dissolving the axial base and the oxygen carrier when they are present together, said axial base being capable of providing a coordinating atom to the oxygen carrier, and said oxygen carrier being a metal-containing complex having any of the structures



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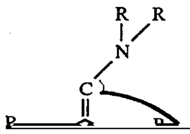
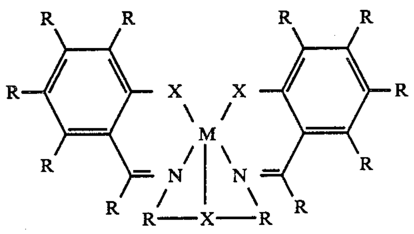
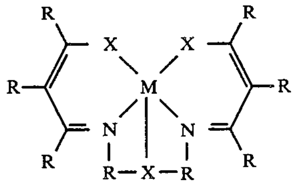


[redacted]

(c) collecting oxygen from the product-stream side of said membrane and nitrogen from the feed-stream side of said membrane,

(d) said membrane comprising a membrane support which is a nonporous polymeric film or a micropo-[redacted] polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture and pentacoordinate oxygen carrier being in the liquid phase when present together, 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 cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

$-\underset{R}{\underset{|}{P}}-$ or $-\underset{R}{\underset{|}{N}}-$; and

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

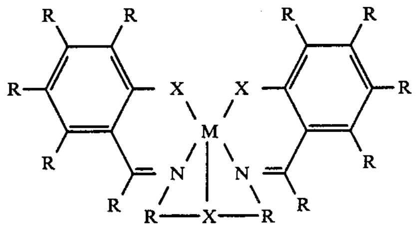
7. A process for the separation and purification of oxygen and nitrogen comprising:

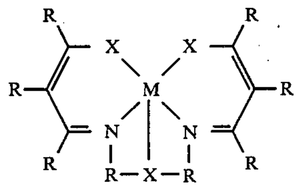
(a) bringing atmospheric air into contact with a membrane, said membrane separating said atmospheric air into a feed stream on one side of said membrane and a product stream on the other side of said membrane,

(b) maintaining the temperature on the product-stream side of said membrane at least approximately 5° C. higher than the temperature on the feed-stream side of said membrane,

(c) collecting oxygen from the product-stream side of said membrane and nitrogen from the feed-stream side of said membrane,

(d) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture and pentacoordinate oxygen carrier being in the liquid phase when present together, 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 cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

$-\underset{R}{\underset{|}{P}}-$ or $-\underset{R}{\underset{|}{N}}-$; and

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

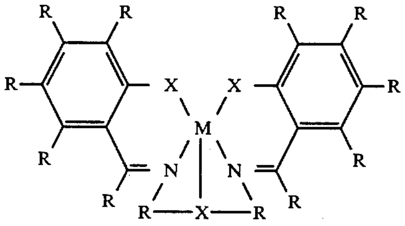
8. A process for the separation and purification of oxygen comprising:

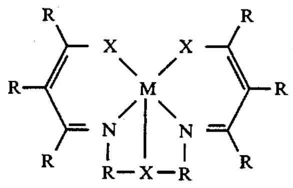
(a) bringing a gaseous oxygen-containing stream into contact with a membrane, said membrane separating said gaseious oxygen-containing stream into a feed stream on one side of said membrane and a product stream on the other side of said membrane,

(b) maintaining the temperature on the product-stream side of said membrane at least approximately 5° C. higher than the temperature on the feed-stream side of said membrane,

(c) collecting oxygen from the product-stream side of said membrane,

(d) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture and pentacoordinate oxygen carrier being in the liquid phase when present together, 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 cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

—P— or —N—; and (each with R attached)

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

9. The process of claims **1**, **2**, **5** or **6** wherein the oxygen partial pressure on the feed-stream side of said membrane is substantially atmospheric or less than atmospheric.

10. The process of claim **1**, **2**, **5** or **6** wherein the oxygen partial pressure on the feed-stream side of said membrane is at least about 10 mmHg higher than atmospheric.

11. The process of claim **1**, **2**, **5** or **6** conducted at a temperature of between about −50° C. and +100° C.

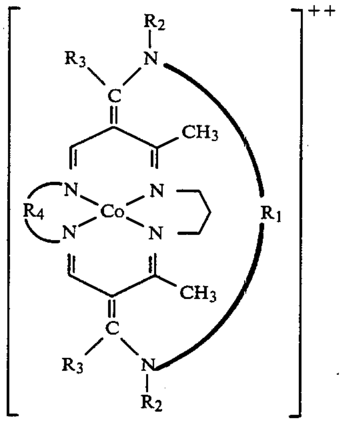
aminopyridine, 4,4-bipyridine, 4-methoxypyridine, 4-methylaminopyridine, 3,4-lutidine, 3,5-lutidine, pyridine, 4-methylpyridine, 4-cyanopyridine, pyrazine, 4-pyrrolidinopyridine and N-methylpyrazinium halides.

16. The process of claim **1**, **2**, **3** or **4** wherein the oxygen carrier is N,N'-bis(salicylideneimino)di-n-propylaminecobalt(II).

17. The process of claim **1**, **2**, **3** or **4** wherein the oxygen carrier is N,N'-bis(3-methoxysalicylidene)ethylenediaminecobalt(II).

18. The process of claim **1**, **2**, **3** or **4** wherein the oxygen carrier is N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

19. The process of claim **1**, **2**, **3** or **4** 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;

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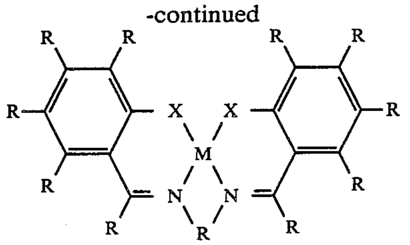
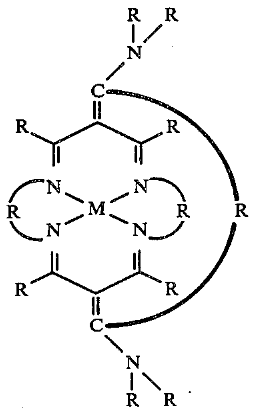
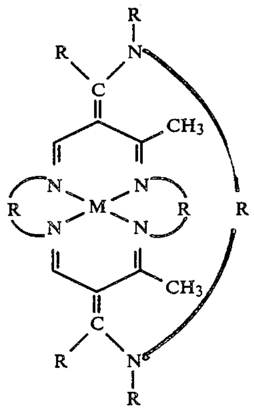
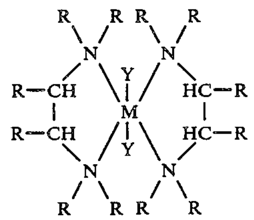




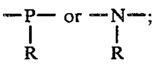




wherein

M is 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.

21. The membrane of claim **20** wherein

the membrane support is a microporous polymeric film selected from polysulfones, polyamides, cellulose derivatives, polyhalogenated hydrocarbons polyesters, polyurethanes, polyolefins polycarbonates, polysaccharides, polyorganosilanes, and polyorganosiloxanes,

the solvent or solvent mixture is selected from lactones, lactams, sulfoxides, nitriles, amines, amides, esters, ethers and other nitrogen-containing liquids, and

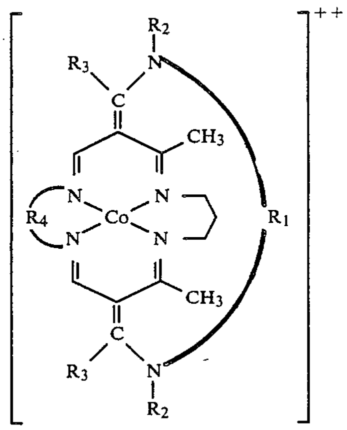
the axial base is selected from Lewis bases containing secondary or tertiary nitrogen atoms, imidazoles, ketones, amides, amines, sulfoxides, pyrazines and pyridines.

22. The membrane of claim **20** wherein

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

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, pyrazine, 4-pyrrolidinopyridine and N-methylpyrazinium halides, and

the oxygen carrier is selected from N,N'-bis(3-methoxysalicylidene)ethylenediaminecobalt(II), N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II), and



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.

23. The membrane of claim **20** wherein the solvent is selected from gamma-butyrolactone and N-methylpyrrolidone and mixtures thereof, the axial base is 4-dimethylaminopyridine and the oxygen carrier is N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

24. The membrane of claim **20** wherein the oxygen carrier is N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II).

25. The membrane of claim **20** wherein the solvent is selected from gamma-butyrolactone and N-methylpyrrolidone and 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).

rous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes,

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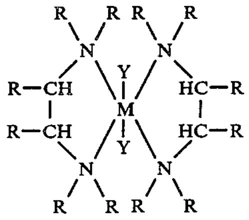


wherein

M is cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

$-\underset{|}{\underset{R}{P}}-$ or $-\underset{|}{\underset{R}{N}}-$;

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

Y is halide, nitrate, thiocyanate or cyanide.

30. Apparatus for the separation and purification of oxygen comprising:

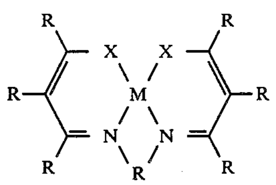
(a) membrane means,

(b) means for bringing a gaseous oxygen-containing stream into contact with said membrane means, said membrane means separating said gaseous oxygen-containing stream into a feed stream on one side of said membrane means and a product stream on the other side of said membrane means,

(c) means for maintaining the oxygen partial pressure on the product-stream side of said membrane means at least approximately 10 mmHg lower than the oxygen partial pressure on the feed-stream side of said membrane means,

(d) means for collecting oxygen from the product-stream side of said membrane means,

(e) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent, an axial base, an oxygen carrier, said solvent or solvent mixture, axial base and oxygen carrier being in the liquid phase when present together, said solvent or solvent mixture being capable of dissolving the axial base and the oxygen carrier when they are present together, said axial base being capable of providing a coordinating atom to the oxygen carrier, and said oxygen carrier being a metal-containing complex having any of the structures



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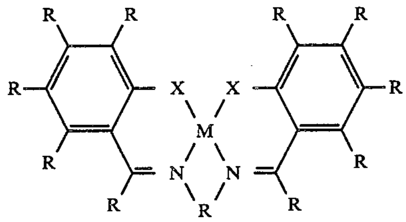

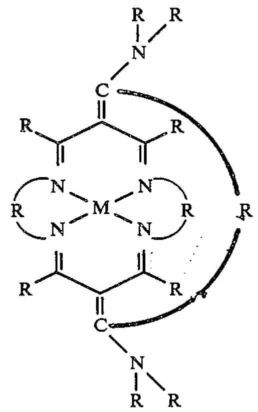

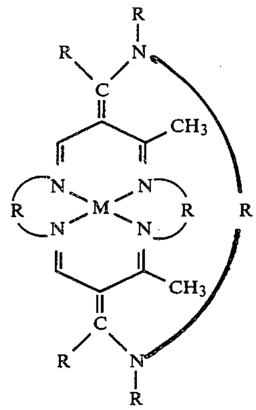

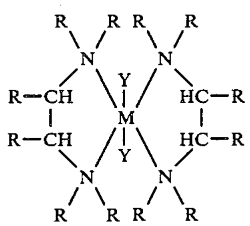

wherein

M is cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

$-\underset{|}{\underset{R}{P}}-$ or $-\underset{|}{\underset{R}{N}}-$;

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

Y is halide, nitrate, thiocyanate or cyanide.

31. Apparatus for the separation and purification of oxygen and nitrogen comprising:

(a) membrane means,

(b) means for bringing atmospheric air into contact with said membrane means, said membrane means separating said atmospheric air into a feed stream on one side of said membrane means and a product stream on the other side of said membrane means,

(c) temperature maintenance means for maintaining the temperature on the product stream side of said

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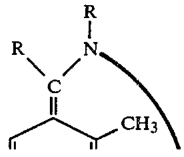
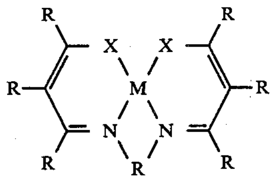
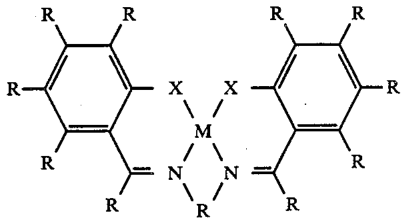
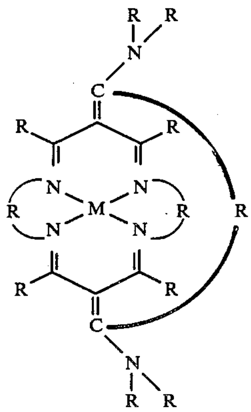
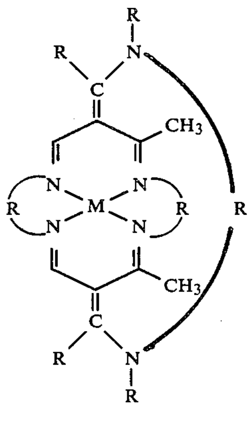


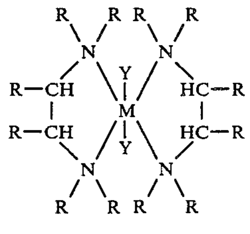
carrier when they are present together, said axial base being capable of providing a coordinating atom to the oxygen carrier, and said oxygen carrier being a metal-containing complex having any of the structures











wherein

M is cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

—P(R)— or —N(R)—;

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

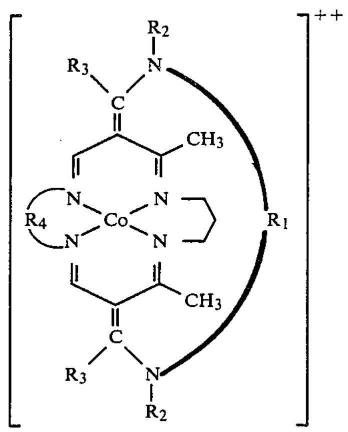
Y is halide, nitrate, thiocyanate or cyanide.

33. The apparatus of claim 29, 30, 31 or 32 wherein the metal is cobalt.

34. The apparatus of claim 29, 30, 31 or 32 wherein the solvent or solvent mixture is selected from at least one of gamma-butyrolactone, dimethylsulfoxide, propylene carbonate, diethylsulfoxide, N-methylpyrrolidone, dimethylacetamide, gamma-valerolactone, delta-valerolactone, epsilon-caprolactone, tributylphosphate, dimethylformamide, diglyme and benzonitrile,

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, pyrazine, 4-pyrrolidinopyridine and N-methylpyrazinium halides, and

the oxygen carrier is selected from N,N'-bis(3-methoxysalicylidene)ethylenediaminecobalt(II), N,N'-bis(3-methoxysalicylidene)tetramethylethylenediaminecobalt(II), and



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.

35. Apparatus for the separation and purification of oxygen and nitrogen comprising:

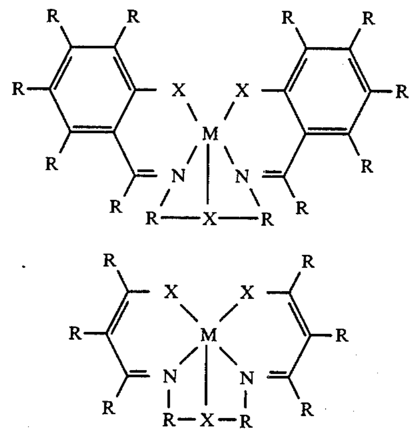
(a) membrane means,

(b) means for bringing atmospheric air into contact with said membrane means, said membrane means separating said atmospheric air into a feed stream on one side of said membrane means and a product stream on the other side of said membrane means,

(c) means for maintaining the oxygen partial pressure on the product-stream side of said membrane means at least approximately 10 mmHg lower than the oxygen partial pressure on the feed-stream side of said membrane means,

(d) means for collecting oxygen from the product-stream side of said membrane means and nitrogen from the feed-stream side of said membrane means,

(e) said membrane comprising a membrane support which is a nonporous polymeric film or a microporous polymeric film selected from polysulfones, polyamides, regenerated cellulose, polyhalogenated hydrocarbons, polyesters, polyurethanes, polyolefins, polycarbonates, polysachharides, polyorganosilanes, and polyorganosiloxanes, said membrane support containing a solvent or solvent mixture and a pentacoordinate oxygen carrier, said solvent or solvent mixture and pentacoordinate oxygen carrier being in the liquid phase when present together, 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 cobalt, iron, copper, nickel, manganese, ruthenium or rhodium;

X is —O—, —S—,

$$-\underset{\displaystyle R}{\overset{|}{P}}- \text{ or } -\underset{\displaystyle R}{\overset{|}{N}}-\text{; and}$$

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

36. The apparatus of claim 34 wherein the oxygen carrier is N,N'-bis(salicylideneimino)di-n-propylaminecobalt(II).

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