

Process for the purification of non-reacting gases

The present invention relates to the purification of certain gas streams and, more particularly, to the purification of such gas streams by the removal of minute quantities of impurities therefrom.

The reaction of basic alkali or alkaline earth metals *per se*, or as hydroxides or weak acid salts, with acids is known chemistry. Such chemistry, as elementary as it may seem, has become the foundation of significant commercial practices. For example, in the field of purifying industrial gas streams, such as hydrogen, carbon monoxide, air, oxygen, nitrogen, argon, helium, lower mono-olefins, lower diolefins, and the like, beds or suspensions of solid particles of sodium or potassium hydroxides have been employed to remove gross amounts of acid gases. Such processes were discovered to be relatively inefficient in removing trace amounts of impurities, such as hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide and mercaptans and the like from such streams. Indeed, such alkali metal hydroxides have been taught for use as absorbents to separate acetylene from ethylene, see US—A—2,742,517.

There is described in US—A—2,185,332, patented January 2, 1940, a process for dehydrating and acid sequestering of refrigeration systems by supplying to the refrigeration systems an alkali alcoholate, particularly sodium methylolate. The alcoholate is supplied to the system to remove water by a methathesis reaction which yields the alkali hydroxide, such as sodium hydroxide. Sodium hydroxide, or caustic, is left in the system. The consequences are obvious. Caustic is a corrosive agent and its presence in the refrigerant gas cannot be beneficial in the long run. In addition, the patent speaks of removing acids as well. For example, hydrogen chloride, presumably as hydrochloric acid, is converted to sodium chloride. It may be that HCl is more corrosive than NaCl, but certainly NaCl is not advantageous to leave in the refrigerant gas. Thus, this patent utilizes known chemistry to solve one problem, but the patent's process creates other problems. As bad a problem that water may be, caustic formation cannot be perceived as a significant improvement.

US—A—2,177,068, patented October 24, 1939, is concerned with the treatment of natural gas to remove water and acid gases. The patent utilizes polyhydric alcohols in combination with amines, e.g., alkanol amines, for this purpose. The patent acknowledges that it was old, even then, to use such amines to remove acid gases, and polyols have long been known as humectants.

In the above two processes, the gases being treated are saturated hydrocarbons whose inertness has been well established. The impurities being removed do not adversely affect the function of these gases; they only adversely affect the environment in which the gases are used.

In any event, the process of this patent suffers from the reliance upon amines to extract the acid gases. These amine systems are known to be corrosive.

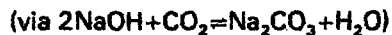
In DE—B—2,333,708 a purification process is disclosed for the selective removal of hydrogen sulfide from hydrocarbon gases employing triethylene glycol as the solvent. No statement or suggestion is made in this reference of the employment of an alkali or alkaline earth metal, hydroxide or other compound in the triethylene glycol solvent, as is required in the process of the present invention for the purification of non-reacting gases. US—A—3,299,163 discloses a process for the removal of unsaturated hydrocarbons from an admixture with conjugated dienes employing generally the same solvent as employed in the process of the present invention. The only significance of this reference is that the solvents are similar. There is, however, no similarity in the materials removed as contaminants from the feedstock stream of the reference, as against the trace impurities removed from the feedstock stream of the present process. In addition, the separation step is carried out in the reference process at a temperature above 100°C, whereas the process of the present invention is carried out at a temperature between 15° and 100°C.

The evolution of industrial gas purification has followed the improvements in impurity detection. With improved analytical procedures that can be applied to the evaluation of industrial gas streams has come the need for superior processes for the removal of newly detectable impurities.

As employed herein, the terms "non-reacting" and "inert gases" refer to those industrial gases which are capable of treatment in accordance with the process of the invention without reacting with the selected alkali/polyhydric alcohol solutions defined below.

It is generally understood that olefins, due to their manner of production, storage and/or handling, may typically contain in trace amounts in the range of parts per million of some or all of the following impurities: water vapor, hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide, and mercaptans. Many commercial syntheses require an olefin feed having below 1, and preferably below 0.5 ppm of each of the impurities.

For example, in order to make suitable grade ethylene for the production of certain grades of polyethylene, small concentrations of CO₂ (of approximately 10—25 ppm) in the olefin feed have to be reduced to less than 1 ppm. One present practice uses a caustic pellet absorber bed. Two major problems associated with this procedure are: (i) only about 3 percent of the NaOH present in the bed is converted to Na₂CO₃



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and (ii) after the outer coat of the pellet is converted to the carbonate, the water generated can cause particle agglomeration and bridging which in turn causes channeling and finally complete solidification of the bed. The latter is a particularly difficult problem because the bed contents at times have had to be removed manually. An aqueous caustic solution has been proposed as an alternative. One problem with this approach is that the water vapor from the solution is introduced into the ethylene, thus necessitating zeolite water-adsorption beds which: (i) would be large and costly to instal; and (ii) would be expensive to regenerate.

The process of this invention employs a liquid, essentially non-aqueous treating medium, that is, the medium typically does not contribute more water to the gas undergoing treatment. The liquid treating medium exhibits (i) a high capacity (i.e., solubility) for the alkali, (ii) a very low vapor pressure, (iii) when combined with the alkali, the system is chemically stable, and (iv) a sufficiently low viscosity to permit proper wetting of the gas being treated.

The process of this invention is the use of an alkali (or alkaline earth) metal/liquid polyhydric alcohol solution to remove the aforedefined trace impurities, and, in particular, simultaneously to remove substantially all of the deleterious trace impurities when they are present, rather than just a single impurity, as has been prior art approach.

Thus, in accordance with the present invention, a process is provided for the purification of an industrial gas stream of hydrogen, carbon monoxide, air, nitrogen, oxygen, helium, argon, mono-olefins having from two to five carbon atoms per molecule, diolefins having four or five carbon atoms per molecule, paraffins, or acetylenes, by the removal of trace amounts of impurities therein, of one or more of water, hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide, hydrogen chloride, hydrogen cyanide, nitric acid, and mercaptans which comprises contacting the said gas, at a temperature between 15 and 100°C, with an essentially non-aqueous liquid solution comprising from 0.5 to 15 weight percent of alkali or alkaline earth metal, in a liquid aliphatic polyhydric alcohol having a carbon to oxygen ratio of one (1) to five (5), and at least two (2) oxygens thereof being separated by not more than two (2) sequential carbon atoms.

In addition, the process of this invention comprises continuously feeding an industrial gas stream, as described, to a body of liquid alkali/polyhydric alcohol solution, as described herein, maintained at a temperature between 15° and 100°C, in which the gas stream is removed from contact with the body into an atmosphere in which the partial pressure of water therein is insufficient significantly to increase the water concentration in the stream. In the preferred embodiment, the water concentration of the stream removed from the liquid body and the atmosphere is less than was contained in the stream fed to the body.

The "alkali and alkaline earth metals" referred to herein are those from groups IA, and IIA of the Period Table of Elements; specifically they are: lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium. As discussed hereinbelow, the preferred alkali metals are sodium and potassium, with potassium constituting the most preferred metal for the practice of the process of the present invention. For purposes of discussion only, the term "alkali" shall mean alkali metal and alkaline earth metal as hereinabove defined.

For brevity in description and for convenience, the process of the invention is primarily discussed hereinbelow in connection with the removal of trace amounts of impurities of the group set forth hereinabove from ethylene gas.

The alkali value provided in the polyhydric alcohol solution may be obtained from the hydroxides and weak inorganic acids of the alkali or alkaline earth metals.

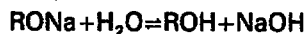
The polyhydric alcohol includes glycerol and alkylene glycols, for example, those having up to twelve carbon atoms (such as: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, 1,2-butylene glycol and di-1,2-butylene glycol), and alkylene oxide adducts. Such alkylene oxide adducts are made by reacting the alkylene oxide with a polyol such as the aforementioned glycols, glycerol and other triols (for example, 1,2,6-hexane triol, monomethyl ether of erythritol, and the monomethyl ether of pentaerythritol). Ethylene oxide and propylene oxide adducts of the polyols are preferred. Most preferred of the adducts are the ethylene oxide adduct, alone or reacted with propylene oxide.

The process of the present invention is for the purification of a gas stream which contains as its major component an inert gas which does not react chemically (non-reacting) with the liquid alkali/polyhydric alcohol solution selected for the process and which stream contains, in trace amounts, a minor component which chemically reacts with the same liquid alkali/polyhydric alcohol solution. Examples of the non-reacting major gas components are: hydrogen; carbon monoxide; air; oxygen; nitrogen; helium; argon; lower mono-olefins, lower diolefins and derivatives thereof; paraffins, such as methane and ethane; and acetylenes. "Olefins" referred to herein are understood to be those selected from the group consisting of mono-olefins having from two to five carbon atoms per molecule, diolefins having from four to five carbon atoms per molecule and derivatives thereof. Typical of such olefins are ethylene, propylene, the butylenes, the pentylenes, 1,3-butadiene, 1,4-pentadiene and derivatives thereof.

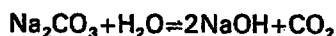
The reacting components or impurities are primarily those which form acids in aqueous solutions. These materials react with the alkali of the solvent to form inorganic or organic salts therewith, thereby

providing an effective means of their removal from the gas. These impurities are hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide, mercaptans, hydrogen chloride, hydrogen cyanide, and nitric acid.

It has been found in practicing this process that water vapor may be simultaneously removed from the feed gas material even though it is usually present in quantities much higher than trace quantities. The removal of water vapor with the alkali/polyhydric alcohol solution is believed to follow a completely different mechanism from that followed by the removal of the trace quantities of the reacting components of the feed material. The mechanism for water removal may be based on the humectant properties of the polyhydric alcohols. In addition, it is believed that further solution capacity can be effected by such metathesis reactions as:



and



It has additionally been found that water removal by the alkali/polyhydric alcohol solution can be effected with respect to contained water in the industrial gas stream which is present up to the limits of saturation in the stream (viz. dew point). The hygroscopicity quality of the polyhydric alcohol which induces water absorption (via hydrogen bonding mechanism) has been found not to diminish the capacity of the alkali/polyol solution for reaction of the solution with other reacting components in trace amounts listed above. Thus, such reactions which involve the reacting component in which water can become an equilibrium component seem not to be adversely affected by the presence of such large amounts of water in the solution.

Accordingly, it is understood that any relatively small amount of water vapor contained in the non-reacting gas feed (introduced therein prior to or during a process for the production or treatment of the non-reacting gas) is scavenged by the polyhydric alcohol and alkali of the absorbent solution. Similarly, any water of reaction formed *in situ* is also scavenged by the alkali solution components as it is found. Thus, the absorbent solution is characterized herein as an "essentially non-aqueous" solution during the period in the process of the invention when it is acting to effect purification by removal of trace amounts of reacting impurities from the non-reacting gas stream.

It should be noted in passing that the partial pressure of water maintained in the vapor phase above the absorbent solution is lower than that in the non-reacting gas stream (mole basis), so that water is not re-introduced into the non-reacting gas stream.

The typical, non-aqueous absorbent solutions of the invention may initially be prepared by the addition of alkali or alkaline earth metal values to a solution of the selected liquid polyhydric alcohol (glycerol and glycols of the stated group). This addition to the polyhydric alcohol solution may be by the direct addition of alkali metal (such as by the addition of sodium turnings), by the addition of the alkali or alkaline earth metal in the form of its hydroxide, or by the addition of the alkali or alkaline earth metal in the form of its carbonate or bicarbonate, or other similarly weak inorganic acid salts. The addition in the metal or hydroxide or salt form may react in a desired manner to form the polyhydric alcoholate of the alkali or alkaline earth metal. It may be that a carbonate form is first hydrolyzed by water to the hydroxide before alcoholate formation.

The alkali/polyhydric alcohol solutions are formed by simply mixing the alkali component with the polyhydric alcohol component until a solution of the two components is formed. This can be done at room temperature or at elevated temperatures, viz. temperatures as high as the boiling point of the alcohol. Normally, mixing between the two components is effected at temperatures of from 30°C to 250°C, preferably at temperatures of from 40°C to 220°C.

The alkali value supplied to the polyhydric alcohol may be in the form of the hydroxide, and as salts of weak inorganic acids, viz. carbonic acid, preferably, the alkali is supplied as the hydroxide, the carbonate and/or the bicarbonate. As pointed out below, the greatest efficiency of impurity removal typically when the alkali is employed as the hydroxide, but that the most stable system is achieved with the carbonate. Illustrative of suitable alkali are, by way of example only, lithium hydroxide, lithium carbonate, lithium bicarbonate, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide, potassium carbonate, potassium bicarbonate, rubidium hydroxide, rubidium carbonate, rubidium bicarbonate, cesium hydroxide, cesium carbonate, cesium bicarbonate, magnesium hydroxide, magnesium carbonate, magnesium bicarbonate, calcium hydroxide, calcium carbonate, calcium bicarbonate, strontium hydroxide, strontium carbonate, barium hydroxide, barium carbonate, and barium bicarbonate.

It has been found that addition of from 0.5 to 15 weight percent of contained alkali or alkaline earth metal values may be employed to form an operable non-aqueous absorbent solution having a satisfactory contained salt concentration, after reaction with a minor portion of the liquid polyhydric alcohol (glycerol or selected glycol), presuming salt formation. It has additionally been found that elevation to a temperature of the order of about 200°C is desirable to effect an activation of the carbonate to the hydroxide form. The alkali, in the hydroxide form, may enter in to an equilibrium reaction which generates the alcoholate and a small amount of water. Whether such alcoholates

contribute to the process of this invention is hard to determine, but it is believed alcoholate formation plays a significant role.

To develop process design data and to study the characteristics of the column operation, a high-pressure pilot unit was constructed. An Oldershaw (Registered Trade Mark) type glass column, 28 mm ID, containing 20 trays was employed. The glass column was mounted in a pressure gauge (Jergusen Co.) for high-pressure operations. The feed gas (ethylene) was preheated to the desired column temperature in a shell-and-tube heat exchanger. Another heat exchanger between the circulating pump and the column was used to control the temperature of the liquid entering the top of the column.

Caustic/glycol solutions were prepared by feeding the desired amounts of sodium hydroxide into the glycol in a mix tank. The solution was stirred at 50–75°C under nitrogen purge. Three hours of stirring was sufficient to dissolve the caustic pellets completely. The solution was then transferred to the reservoir section of the Oldershaw column for water stripping. The solution was circulated at 50°C 344.75 kN/m² (50 psig), with nitrogen gas flowing countercurrent to the liquid flow. The stripping was continued until the water concentration in the purge nitrogen decreased below 10 ppm.

The Oldershaw column contained three sample taps to analyze the gas entering and leaving the column. The gas samples were continuously analyzed for CO₂ and H₂O. Also periodic liquid samples were taken for viscosity determinations.

The column was tested under a variety of operating conditions. These tests can be summarized as follows:

20	Solvents:	Ethylene glycol Triethylene glycol (TEG)
	Reactants:*	2% (wt) NaOH or 5% (wt) NaOH 2% Pyrogallol 2% MnCl ₂ N ₂ or C ₂ H ₄ (100–365) 689.5–2516.7 38–60°C 0.023–0.167 (0.15–0.30) 45.7–91.4
25	Feed gas:	
	Column pressure, (psig):	
30	kN/m ²	
	Column temperature, °C:	
	Liquid-to-gas mass flow ratio:	
	Gas velocity, (ft/sec):	
	mm/sec	
35	CO ₂ Concentration in feed gas, ppm:	1–110
	H ₂ O Concentration in discharge gas, ppm:	1–1000
	O ₂ Concentration in feed gas, ppm:	0–50
	H ₂ S Concentration in feed gas, ppm:	0–20

*Reactant weight percent based on the weight of the total solution.

For good gas-liquid contacting and stable operation, the gas velocity should not exceed the column flooding velocity. Flooding velocities were calculated using a typical correlation for sieve towers for 5 percent NaOH/TEG solutions as set forth in Table I:

TABLE I
Flooding velocities for Oldershaw column

50	Solution: 5 percent NaOH/TEG Gas: C ₂ H ₄ Column diameter: 28 mm			
55	Liquid-to-Gas mass flow ratio*	Column pressure, kN/m ² (psig)	Column temperature, °C	Flooding velocity* m/sec (ft/sec)
	0.1	2068.5 (300)	20	0.329 (1.08)
	0.2	2068.5 (300)	20	0.296 (0.97)
60	0.1	2758.0 (400)	20	0.344 (1.13)
	0.2	2758.0 (400)	20	0.320 (1.05)
	0.1	103.4 (15)	75	1.524 (5)
	0.2	103.4 (15)	75	1.372 (4.5)
	0.1	729.5 (115)	40	0.549 (1.8)

*Based on total cross-sectional area of the tower.

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For column operation above 1723.7 kN/m² (250 psig), the calculated flooding velocity is about 0.305 m/sec (1.0 ft/sec). The data base for this correlation consists of mostly industrial operations with aqueous solutions, and thus, liquid viscosity is not included in the correlation. Therefore, its applicability to a viscous medium such as caustic/glycol solutions is uncertain. The pilot unit was operated at gas velocities 45.7 to 91.4 mm/sec (0.15 to 0.30 ft/sec). When the gas velocity exceeded 213.4 mm/sec (0.7 ft/sec) column operations became unstable. This value corresponds to roughly 60 percent of the calculated flooded velocity, suggesting that the flooding velocity correlations should be adjusted for viscosity.

With both ethylene glycol and triethylene glycol/caustic solutions, tray action was excellent in the indicated operating range.

The results of the CO₂ removal experiments are set forth in Table II.

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TABLE II
CO₂ Removal with glycol/caustic solutions

Solvent	NaOH wt %	Pressure, kN/m ² (psig)	Temp., °C	** L/G	U _g , mm/sec (ft/sec)	H ₂ O Content in the solution	No. trays	CO ₂ Concentration, ppm	
								Feed	Discharge
EG	5	689.5 (100)	38	0.046	45.7 (0.15)	high	20	40	0.46
EG	5	689.5 (100)	38	0.069	88.4 (0.29)	high	20	80	2.0
EG	2	689.5 (100)	55	0.023	88.4 (0.29)	high	20	45	1.25
EG	2	689.5 (100)	40	0.137	45.7 (0.15)	high	20	85	1.0
TEG	5	689.5 (100)	42	0.046	45.7 (0.15)	high	20	95	0.50
TEG	2	689.5 (100)	52	0.069	88.4 (0.29)	high	10	45	0.27
TEG	2	689.5 (100)	52	0.069	88.4 (0.29)	high	10	112	0.22
TEG	2	689.5 (100)	52	0.069	88.4 (0.29)	high	10	50	0.12
TEG	5	689.5 (100)	50	0.167	39.6 (0.13)	high	10	1.1	0.20*
TEG	5	1379.0 (200)	51	0.109	45.7 (0.15)	low	10	>50	0.30*
TEG	5	1379.0 (200)	50	0.143	45.7 (0.15)	low	10	>50	0.60*
TEG	5	1654.8 (240)	50	0.125	51.8 (0.17)	low	10	43	1.60*
TEG	5	1654.8 (240)	53	0.05	64.0 (0.21)	low	10	12	3*
TEG	5	2516.7 (365)	57	0.036		low	10	41	1.1
TEG	5	2516.7 (365)	57	0.036		low	10	13	0.65

*Same batch running continuously for three weeks

**In mass units

L/G=liquid-to-gas flow rate ratio

U_g=gas velocity through the column

EG=ethylene glycol

TEG=triethylene glycol.

Based on these results, the following was concluded:

1. Both ethylene glycol and triethylene glycol/caustic mixtures are very effective for trace CO₂ removal. Triethylene glycol, however, is preferred due to its lower vapor pressure.
2. It is possible to reduce the CO₂ concentration in ethylene to less than 0.5 ppm with a ten tray column, provided that good gas-liquid contact is maintained.
3. Liquid-to-gas flow rate ratios as low as 0.05 are sufficient for efficient CO₂ removal.
4. Five percent NaOH/TEG solutions flow easily at 40—50°C with good tray action. The viscosity of this solution at 40°C is 110 cps.
5. After three weeks of continuous operation with one batch of 5 percent NaOH/TEG solution, no viscosity increase was observed, even though the solution contained the reaction by-product Na₂CO₃.
6. No Na₂CO₃ solid settling was apparent in the reservoir. However, some solids were trapped in the liquid filters. It appears that the settling velocity is very slow.
7. CO₂ removal was equally efficient before and after the water content of the solution was stripped off.

One batch of 5 percent NaOH/TEG solution was operated continuously for three weeks until the CO₂ concentration in the column discharge started increasing due to decreased NaOH content relative to the total solution. To test whether the decrease in CO₂ removal efficiency is due to lack of free water in the system or due to decreased NaOH content, a pint of TEG containing 0.1 weight percent H₂O was added to the liquid reservoir and the column was restarted. No improvement in CO₂ removal was observed, indicating that the decreased NaOH content was responsible for the decreased column efficiency.

During the lengthy period of continuous operation, three liquid samples were taken for viscosity measurements. No change in viscosity was observed, suggesting the dimerization and oligomerization reactions are insignificant. The same solution was filtered to remove the Na₂CO₃ solids, because no noticeable settling occurred in the liquid reservoir. This observation is consistent with settling velocity calculations using the Stokes equation. These calculations show, for example, for a Na₂CO₃ particle one micron in diameter, the settling velocity is 1.52 mm/day, (0.005 ft/day) at 40°C in 5 percent NaOH/TEG solution. From scanning electron microscopy measurements, Na₂CO₃ particles range in size from 1—10 microns, mostly in the lower size range. These results suggest that a filtration step may be necessary for solids removal.

In addition to the employment of sodium and lithium as alkali metals for the *in situ* reaction with the selected glycol to form the non-aqueous absorbent solution, tests were conducted to determine the effectiveness of loading various glycolates with various alkaline earth metal hydroxides. The following Tables III and IV show, respectively, the loading of equivalent weight percentages of strontium, barium and calcium hydroxides to diethylene glycol, and the resultant carbon dioxide loss and percentage of theoretical carbon dioxide displaced for nine (9) cycles of regeneration employing these alkaline earth metal hydroxides.

Fig. 3 of the drawings set forth a graphical representation of comparative non-aqueous reversible carbon dioxide scavenging efficiency for barium, calcium, potassium and sodium-based systems through the nine cycles of regeneration. It is to be noted that the sodium-based system presents a consistently high efficiency of operation through all nine cycles.

TABLE III
Initial CO₂ loadings in various glycolates

Solvent	Solvent weight, gm	CO ₂ Uptake, gm
5 wt % Sr(OH) ₂ in diethylene glycol	125	1.95
5 wt % Ba(OH) ₂ in diethylene glycol	125	2.80
5 wt % Ca(OH) ₂ in diethylene glycol	125	4.50
Conditions: Room temperature CO ₂ pressure-atm.		

TABLE IV
Regeneration history of alkaline earth metal glycolates

	Solvent	Regeneration cycle	CO ₂ Loss, gm	% Of theoretical CO ₂ displaced
5	5 wt % Sr(OH) ₂ in diethylene glycol	1	0.8	44
		2	0.3	17
		3	0.5	28
10		4	0.9	50
		5	0.4	22
		6	0.4	22
		7	0.4	22
		8	0.3	17
15		9	0.35	19
	5 wt % Ba(OH) ₂ in diethylene glycol	1	0.5	39
		2	0.5	39
		3	0.35	27
20		4	0.45	35
		5	0.4	31
		6	0.5	39
		7	0.5	39
		8	0.45	35
25		9	0.5	39
	5 wt % Ca(OH) ₂ in diethylene glycol	1	1.5	51
		2	1.1	37
		3	1.2	40
30		4	1.05	35
		5	1.0	34
		6	1.2	40
		7	1.0	34
		8	0.9	30
35		9	0.95	32

Conditions: CO₂ addition at 1 atm and room temperature
Regeneration at 200°C
Solvent weight—125 gm

In the drawings:—

Fig. 1 is a simplified schematic flow sheet of an apparatus arrangement suitable for practicing the process of the invention for gas purification;

Fig. 2 is a schematic flow sheet of an apparatus arrangement similar to that of Fig. 1 and additionally having means for the regeneration of spent non-aqueous absorbent solution and recycling the regenerated solution to the liquid-gas contactor for further use;

Fig. 3 is a curve showing the carbon dioxide displacement efficiency for a number of cycles of thermal regeneration of four different alkali or alkaline earth metal based scavenging systems;

Fig. 4 is a simplified schematic flow sheet for a pilot plant having continuous purification of gas streams with absorbent regeneration wherein no metal carbonate precipitate is formed during operation; and

Fig. 5 is a simplified schematic flow sheet for a pilot plant having continuous purification and cyclic regeneration, wherein insoluble metal carbonate precipitate is formed and removed during operation.

Apparatus suitable for commercial operation of the process of the invention is shown schematically in Fig. 1 of the drawings. As there shown, the contacting device may alternatively be a vessel filled with the caustic (NaOH) extractant solution through which the gas stream to be treated is passed.

In the process of the invention, feed gas containing impurities such as CO₂, H₂O, SO₂, H₂S, COS and mercaptans is mixed with a non-aqueous solution in a gas-liquid contactor containing one or more contacting zones. The impurities are removed from the gas by reaction with or dissolution into the solution. If necessary for purity considerations, the purified gas leaving the gas-liquid contactor may be further treated, e.g., by passing through a selective adsorbent bed, to remove traces of the non-aqueous solution.

Depending on the concentration of impurities in the feed and the amount of feed processed, the

solution may have to be renewed. This can be done intermittently or continuously by (1) removing solid products of reaction, (2) purging spent solution, and/or (3) separating spent solution and absorbed impurities from active solution. To compensate for any removal of solution by the clean-up or by entrainment or vaporization into the purified gas, provision is made for introductions of makeup non-
5 aqueous solution into the process.

A demister may be provided in the top of the column to remove large size spray particles. Ethylene gas leaving the demister passes through a filter which removes sub-micron sized glycol mist. Depending on the size, the liquid can be returned to the stripping still or for small flows it can be connected in a drum and be disposed of periodically. Downstream of the filter, an activated carbon trap
10 may be provided to remove last traces of TEG from ethylene. At 50°C, 3102.75 kN/m² (450 psig), TEG concentration in ethylene will be less than 0.1 ppm. In the event that TEG removal is desired below that level, it is easily accomplished by adsorption with activated carbon. The TEG loading on activated carbon is expected to be greater than 20 percent by weight. At this loading, 0.363 tonnes (800 pounds) of activated carbon is sufficient completely to remove all traces of TEG from a column treating 18.14
15 tonnes/hr (40,000 lbs/hr) ethylene in one year (8000 hrs) of the operation. Therefore, activated carbon can practically be used on a throw-away basis, and no regeneration facilities are needed to allow reasonably economical operation.

A double filter arrangement may be provided to remove the carbonate solids from the solution. The caustic/glycol solution leaving the filters is separated into two streams. Approximately 20 percent
20 of the flow is depressurized to 137.9 kN/m² (20 psig) and routed to the stripping still, and the remaining 80 percent is circulated to the top of the absorber via the circulating pump. For a column treating 18.14 tonnes/hr (40,000 lbs/hr) ethylene, liquid flow should be at least 37.8 l/min (10 gallon/min) (L/G=0.125).

The stripping still operates at 68.95—137.9 kN/m² (10—20 psig), 100°C, and it has two primary
25 functions:

1. To decrease the moisture content of the fresh caustic/glycol solutions to less than 10 ppm in the gas phase. This is accomplished by nitrogen purging at 100°C intermittently when make-up solid caustic is added to the system.
2. To remove the moisture adsorbed by the circulating solution with continuous nitrogen purging
30 at 100°C. With this mode of operation, the caustic/glycol solution will remove CO₂ by reaction and H₂O by physical adsorption. Since the moisture content of the incoming ethylene is small (~5 ppm), only a small portion of the circulating solution needs to be desorbed. The still should be sized to hold 454 l (120 gallons) of 10 percent NaOH/TEG solution.

The stripping still is equipped with a turbine-type agitator to dissolve the solid caustic in glycol
35 solutions. As NaOH is removed from the system by reaction with CO₂, fresh sodium hydroxide must be added. To add solid caustic, the still is depressurized and purged with nitrogen, the tank is opened and flake caustic is added to bring the solution to, for example, 15 percent NaOH. After the moisture content in the purge nitrogen is below 10 ppm this concentrated stream is gradually mixed with the circulating solution. During the solid caustic addition and moisture removal step, all of the liquid leaving
40 the filters is circulated to the column with no side flow to the stripper.

The heat source for the still can be low-pressure steam on the jackets. It should be capable of heating the solution to 150°C, although a maximum of 100°C is sufficient for efficient moisture removal.

The following Table V sets forth typical examples of the practice of the process of the present
45 invention employing varying feed gases, sodium and potassium-based absorbent systems, flow rates and operating temperatures employed.

From the examples set forth herein, it may be seen that, in the process of the present invention, bulk quantities (major proportions of the absorbent) of the glycol/glycolate solution are employed to effect gas purification (of nitrogen or ethylene) by reduction of impurities such as carbon dioxide,
50 carbonyl sulfide, and hydrogen sulfide from a relatively high concentration level to a low parts per million level.

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60

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TABLE V

System wt % caustic/solvent	Feed gas† ppm/gas	Feed flow rate (SCFH) m³/hr	Scrubber temp. °C	Impurity remaining (ppm)	Remarks
10% NaOH/glycerol	10⁴ CO₂/N₂		60	0.2—0.5	Tube with steel wool baffles
10% NaOH/ethylene glycol	10⁴ CO₂/N₂		25	0.2—0.4	Tube with steel wool baffles
20% NaOH/ethylene glycol	10⁴ CO₂/N₂		60	0.3—0.5	Tube with steel wool baffles
5.04% NaOH*/triethylene glycol	500 CO₂/N₂	(24) 0.68	75	<1	Oldershaw column, 20 trays
5% NaOH/triethylene glycol	500 CO₂/N₂	(27) 0.76	75	<1	Oldershaw column, 10 trays
5% NaOH/triethylene glycol	500 CO₂/N₂	(13) 0.37	75	<1	Oldershaw column, 20 trays
2% NaOH/triethylene glycol	500 CO₂/N₂	(27) 0.76	75	3	Oldershaw column, 20 trays
	500 CO₂/N₂	(13) 0.37	75	1.5	Oldershaw column, 20 trays
	500 CO₂/N₂	(27) 0.76	75	5	Oldershaw column, 10 trays
2% NaOH/Triethylene glycol	500 CO₂/N₂			<1	Tube with steel wool baffles
20% KOH/ethylene glycol	10³ CO₂/C₂H₄		25	17—25	
20% KOH/ethylene glycol	10³ COS/C₂H₄			<1	
20% KOH/ethylene glycol	10³ H₂S/C₂H₄			<1	

*Added as 2.9% Na metal.

**Liquid flow in column, 100 g/hr.

†Feed gas pressure-atmospheric.

In a pilot plant of the type shown in the flow sheet of Fig. 5 of the drawings, an on-stream example of the purification process of the invention was carried out. A preliminarily purified ethylene stream from a commercial ethylene production facility was passed for a period of 56 days through a non-aqueous absorbent solution containing 6% sodium hydroxide (94% triethylene glycol) in a non-aqueous scrubber. The scrubber temperature was 30°C and the ethylene feed pressure 3102.75 kN/m² (450 psig). The inlet carbon dioxide range over the period was 1—6 ppm and the outlet carbon dioxide range was 0.05—0.15 ppm. The ethylene feed was 13.6 kg (30 pounds) per hour and the gas velocity in the scrubber was 183 mm (0.6 feet) per minute. The scrubber in the final days of operation was found to reduce an inlet carbon dioxide impurity in the gas stream of 5.35 ppm to an outlet content of 0.10 ppm.

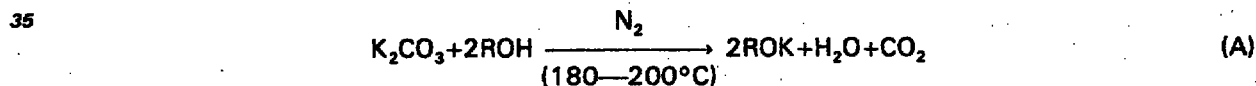
In the initial experimental practice of the process of the invention, a sodium-based system was investigated wherein the absorbent solution was prepared by addition of sodium hydroxide or carbonate, or metallic sodium to the excess glycol or glyceride solution to provide the desired sodium glycol or glyceride salt in unreacted glycol or glycerol solvent.

The process of such sodium-based system can present a problem in stream processing. When employing absorbent solutions based on NaOH and a liquid polyhydric alcohol, there may arise the need for filtration of the spent solution to effect removal of very fine (1—40 microns) Na₂CO₃ solids produced when any moisture is present. The process of the sodium-based system also presents the inherent limitation (when not further treated) of being a one-shot, non-continuous process in terms of the caustic employed.

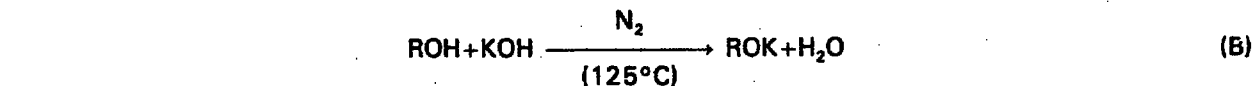
It has been found that a potassium-based absorbent system, as described hereinbelow, provides advantages over the sodium-based absorbent system. The non-aqueous absorbent solution is a potassium glycolate or glycerate formed by the reaction of either elemental potassium, potassium hydroxide or potassium carbonate with the polyol, e.g., glycol and/or glycerol. When the preferred potassium carbonate is employed as the source of potassium, a thermal activation step at about 200°C is desired for optimization of alcoholate formation.

The continuous system is typified by the thermal regeneration of a potassium-based glycolate or glycerate containing solution which are used to scavenge CO₂ from a variety of feed streams. It has been found that K₂CO₃ dissolved in glycol solutions is quite soluble up to concentrations of about 10 weight percent at ambient temperatures or slightly above (viz. 20—25°C). It also has been found that, when these K₂CO₃-continuous solutions are heated to ~180—200°C, the K₂CO₃ decomposes to release CO₂ with the simultaneous formation of a potassium glycolate salt.

The reaction is believed to be:

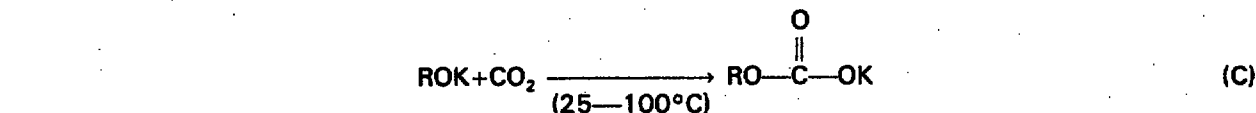


wherein ROH represents any glycol. The potassium glycolate salt, ROK, is therefore of the same species as if it were initially produced from KOH, as follows:



When ROK is formed in the presence of water, due to the use of KOH as the alkali metal source material (see Equation B) the H₂O is scavenged from the system at the regenerator by displacement with N₂ gas.

Upon CO₂ scavenging in the absence of water, the reaction is believed to be as follows:



The product



is also soluble in the excess glycol solvent and will also decompose at 180—200°C to split out CO₂, thus regenerating the ROK salt for re-use. If trace quantities of water enter the scrubber with the feed it is believed that the inorganic carbonate K₂CO₃ will be formed, but unlike the Na₂CO₃ which would be present as a solid, K₂CO₃ remains in solution and can again be thermally regenerated. Hence, the advantage of this aspect of the invention is that under the indicated conditions no precipitate will form

and all carbonate species formed can be thermally decomposed, thus providing a reactivated CO_2 scavenging solution after proper cooling before it is returned to the scrubber section.

This aspect of the invention, therefore, provides a thermally regenerable CO_2 scavenging system without the need for filtration equipment.

5 The $\text{KOH}-\text{K}_2\text{CO}_3$ /glycol process for CO_2 removal is based on the use of stable non-aqueous solvents, such as triethylene glycol, with low vapor pressure and with high dissolving capacity.

The chemistry of $\text{KOH}-\text{K}_2\text{CO}_3$ /glycol solutions is not entirely understood at present. It is not believed that potassium carbonate is simply physically dissolved in glycols. According to our best understanding, some reactions between the alkali and, e.g., triethylene glycol (TEG) is achieved; 10 probably a partial alcoholation is effected.

Commercially available triethylene glycol (TEG) contains about 0.1 percent (weight) water. In addition, KOH/TEG reactions form water. Therefore, when a glycolate or glycerate is prepared, the mixture will contain some water after preparation. This water is typically stripped away, prior to use of the solution for impurities removal. During the stripping operation, the equilibrium will continuously 15 shift to the right as the water is removed from the system favoring alcoholate formation. If the major portion of the water is removed from the system, the solution will contain potassium glycolate, unreacted glycol and small amounts of free unreacted KOH and/or K_2CO_3 (if used as a starting material). The KOH/glycol solutions are extremely hygroscopic and there will be some chemically condensed water complexed with the excess glycol and remain in the solution even following the drying step. This 20 water is removed from the system by heating and purging with an inert gas or by an equivalent means and is not permitted to accumulate. However, such water removal is not critical to the invention. Thus, the KOH/glycol solutions also can function as water scavengers.

Table V hereinabove sets forth typical examples of the practice of the process of the invention employing varying feed gases, NaOH and $\text{KOH}/\text{solvent}$ systems, flow rates and operating temperatures 25 employed.

From the examples set forth, it may be seen that, in the process of the invention, bulk quantities (major proportions of the absorbent) of the glycol/glycolate solution are employed to effect gas purification (of nitrogen or ethylene) by reduction of impurities such as carbon dioxide, carbonyl sulfide, and hydrogen sulfide from a relatively high concentration level to a low parts per million level.

30 The use of the potassium-based system adds improved water scavenging capabilities simultaneously with its application as CO_2 scavenger, such being accomplished without solids forming. In case of the ethylene feed which also contains trace amounts of water, this system eliminates the need for water-removing adsorbents or at least reduces their size considerably. One ideal application is for the removal of atmospheric CO_2 and H_2O from air feed in the production of N_2 and O_2 by cryogenic 35 air separation.

As discussed hereinabove, the spent non-aqueous absorbent solution is regenerated in the cyclic process as is graphically shown in the flow sheet of Fig. 2 of the drawings. As there shown, a nitrogen gas purge is employed in the solution regeneration step in combination with heating to a temperature of about $180-200^\circ\text{C}$ to decompose (to carbon dioxide) the carbonate formed in the solution and 40 remove the carbon dioxide along with water vapor and other vapor impurities which are released and purged.

As indicated hereinabove, the flow sheet set forth in Fig. 4 of the drawings shows a cycle embodying the process of the invention for the potassium-based system or any other system in which insoluble, solid carbonate precipitate is not formed in the absorbent solution. As there shown, valves 45 V1 and V2 would be open only for a fraction of daily, continuous operation. The cycle will permit a batch or continuous regeneration operation. If continuous, a cooler is required in the line between the makeup and regeneration vessel and the storage vessel. It is to be noted that the solution is cooled in the regeneration vessel prior to transfer to the storage vessel. The embodiment of this figure of the drawings is designed to operate for the purification of ethylene, employing 6% by weight K_2CO_3 feed in 50 triethylene glycol solution. The use of nitrogen purge gas for evolved CO_2 and other vapor impurities is optional with this potassium-based system.

The use of a sodium-based non-aqueous absorbent solution for extended time periods can result in the formation of fine sodium carbonate precipitate particles (of the order of 1—40 microns in size), making the removal of the precipitate merely by employment of a filtration step more difficult. It has 55 been determined that such fine precipitate may be agglomerated into particles of larger size (of the order of 200—400 microns) by a number of alternative processing steps. Such larger precipitate particles can then be removed from the solution by the use of a simple direct filtration step, as indicated in the embodiment of apparatus shown in Fig. 5 of the drawings.

This agglomeration can be effected by any one of a number of procedures such as: the addition of 60 up to 15% by weight of water prior to heat treatment at about 150°C ; and the addition of up to 2% by weight of common ion addition (e.g., sodium chloride for chloride ion), with or without up to about 5% by weight water. Such additions to the cycle to effect agglomeration are not shown in the simplified flow sheet of Fig. 5 but may be made along with the used of a related heated in the line immediately 65 upstream of the filter press.

The NaOH -based non-aqueous scrubber has the disadvantage that a precipitate, Na_2CO_3 , tends to

accumulate under certain operating conditions. However, the NaOH-based non-aqueous scrubber is still more attractive when compared to the NaOH solid pellet absorber system. As indicated hereinabove, it was found that the use of the K_2CO_3 -based non-aqueous scrubber resulted in a thermally regenerable system. The K_2CO_3 system has two distinct advantages over the NaOH system in that it is free of precipitation of solids upon CO_2 cycling and it is more thermally stable. However, the K_2CO_3 has only about half the chemical efficiency as the NaOH system for cyclic CO_2 scavenging. Earlier studies indicated that NaOH-based systems can displace approximately 42% of the theoretical amount of CO_2 absorbed while K_2CO_3 -based systems displace approximately 20% CO_2 .

Table VI summarizes the results of cyclic CO_2 scrubbing using solutions consisting of 3 weight percent LiOH dissolved in diethylene, triethylene, and dipropylene glycol. Theoretically, 5.5 grams of CO_2 can be absorbed by 100 grams of 3 weight percent LiOH in these solvents, based on the organic carbonate stoichiometry. Using 5.5 grams as a figure for total CO_2 absorption, one can calculate theoretically the percent CO_2 displaced for each CO_2 absorption/desorption cycle. Through five cycles of CO_2 absorption/desorption, 3 weight percent LiOH/diethylene glycol theoretically displaced an average 14.7% of the theoretical amount of CO_2 per cycle while the LiOH-based solutions of dipropylene and triethylene glycol respectively, displaced an average 15.7 and 14.3% of the theoretical amount of CO_2 per cycle. From a standpoint of efficient CO_2 displacement, this study shows there is little if any significance in selecting one LiOH-based glycol solution in preference to another. Furthermore, from Table VI, it is seen that CO_2 displacement (i.e., chemical) efficiency declined drastically with each succeeding cycle of CO_2 absorption/desorption, regardless of glycol selection. For comparative purposes, Table VII shows the results for NaOH, K_2CO_3 and LiOH-based non-aqueous solutions of diethylene glycol. From Table VII the NaOH-based, non-aqueous scrubber appears to have superior chemical efficiency compared to K_2CO_3 and LiOH-based non-aqueous scrubber. This conclusion is supported by the fact that after five cycles of CO_2 cycling, NaOH theoretically displaces a mean value of 42.0% of the theoretical amount of CO_2 per cycle while K_2CO_3 and LiOH-based non-aqueous scrubbers displace 19.9 and 17.4% respectively, per cycle.

TABLE VI
Non-aqueous reversible CO_2 scavenging using 3 wt % LiOH in glycol solvents (regeneration temperatures 200°C)

Solvent	Regeneration cycle	CO_2 Loss (grams)	Theoretical % CO_2 displaced	
Diethylene glycol	1	1.60	29.1	Theoretical % CO_2 displaced after 5 cycles $\bar{X}=17.4\%$
	2	1.30	23.6	
	3	1.10	20.0	
	4	0.50	9.09	
	5	0.30	5.45	
Triethylene glycol	1	1.00	18.2	Theoretical % CO_2 displaced after 5 cycles $\bar{X}=14.3\%$
	2	0.90	16.3	
	3	0.90	16.3	
	4	0.60	10.9	
	5	0.55	10.0	
	6	0.60	10.9	
	7	0.90	16.3	
	8	0.40	7.27	
Dipropylene glycol	1	0.90	16.3	Theoretical % CO_2 displaced after 5 cycles $\bar{X}=15.9\%$
	2	1.10	20.0	
	3	1.00	18.2	
	4	0.90	16.3	
	5	0.50	9.09	
	6	0.60	10.9	
	7	1.03	18.7	
	8	0.50	9.09	

TABLE VII

Comparative non-aqueous reversible CO₂ scavenging efficiency for Na, K, and Li based systems

	Caustic	Solvent	Regeneration cycle	CO ₂ Loss grams	Theoretical % CO ₂ displaced	Theoretical % CO ₂ displaced $\bar{X}$ value
5	5 Wt % NaOH	Diethylene glycol	1	2.70	49.1	42.0
			2	2.45	44.5	
			3	2.20	40.0	
10			4	2.00	36.4	
			5	2.20	40.0	
	7 Wt % K ₂ CO ₃	Diethylene glycol	1	0.74	16.6	19.9
			2	1.67	37.4	
15			3	0.84	18.8	
			4	0.99	22.2	
			5	0.20	4.48	
	3 Wt % LiOH	Diethylene glycol	1	1.60	29.1	17.4
20			2	1.30	23.6	
			3	1.10	20.0	
			4	0.50	9.07	
			5	0.30	5.45	

Claims

1. A process for the purification of an industrial gas stream of hydrogen, carbon monoxide, air, nitrogen, oxygen, helium, argon, mono-olefins having from two to five carbon atoms per molecule, diolefins having four or five carbon atoms per molecule, paraffins, or acetylenes, by the removal of trace amounts of impurities therein, of one or more of water, hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide, hydrogen chloride, hydrogen cyanide, nitric acid, and mercaptans which comprises contacting the said gas, at a temperature between 15 and 100°C, with a liquid essentially non-aqueous solution comprising from 0.5 to 15 weight percent of alkali or alkaline earth metal, in a liquid aliphatic polyhydric alcohol having a carbon to oxygen ratio of one to five, and at least two oxygens thereof being separated by not more than two sequential carbon atoms.
2. A process in accordance with claim 1, wherein the gas stream contains dissolved water vapour in an amount up to its limit of saturation therein, the water vapor being concurrently removed from the gas stream with other of such impurities.
3. A process in accordance with claim 1, wherein the concentration of the alkali metal is from 1 to 10 weight percent.
4. A process in accordance with claim 1, wherein the alkali or alkaline earth metal is sodium or potassium provided as the hydroxide.
5. A process in accordance with claim 4, wherein the alkali metal hydroxide is sodium hydroxide.
6. A process in accordance with claim 1, wherein the alkali metal or alkaline earth metal is potassium provided as the hydroxide or carbonate.
7. A process in accordance with claim 1, wherein the selected gas is ethylene.
8. A process in accordance with claim 1, wherein the selected polyhydric alcohol is triethylene glycol.
9. A process in accordance with claim 1, wherein the stream is continuously fed to a liquid body of the solution, the gas stream is removed from contact with the body into an atmosphere contiguous with the body in which the partial pressure of water vapor therein is insufficient significantly to increase the water concentration in the stream.
10. A process in accordance with claim 9, wherein the water concentration in the stream leaving the body and the atmosphere is less than that contained in the stream fed to the body.
11. A process in accordance with claim 10, wherein the alkali and alkaline earth metal is potassium provided as a carbonate.
12. A process in accordance with claim 1, wherein the solution is regenerated periodically by thermal treatment.
13. A process in accordance with claim 12, wherein the thermal treatment is heating to a temperature to from 180 to 200°C.
14. A process in accordance with claim 1, wherein the contacting involves countercurrently passing the stream through the solution.

Patentansprüche

1. Verfahren zur Reinigung eines industriellen Gasstromes von Wasserstoff, Kohlenmonoxid, Luft, Stickstoff, Sauerstoff, Helium, Argon Monoolefinen mit 2 bis 5 Kohlenstoffatomen pro Molekül,

TABLE VII

Comparative non-aqueous reversible CO₂ scavenging efficiency for Na, K, and Li based system

	Caustic	Solvent	Regeneration cycle	CO ₂ Loss grams	Theoretical % CO ₂ displaced	Theoretical % C displaced $\bar{X}$ value
5	5 Wt % NaOH	Diethylene glycol	1	2.70	49.1	42.0
			2	2.45	44.5	
			3	2.20	40.0	
			4	2.00	36.4	
10			5	2.20	40.0	
	7 Wt % K ₂ CO ₃	Diethylene glycol	1	0.74	16.6	19.9
			2	1.67	37.4	
			3	0.84	18.8	
15			4	0.99	22.2	
			5	0.20	4.48	
	3 Wt % LiOH	Diethylene glycol	1	1.60	29.1	17.4
20			2	1.30	23.6	
			3	1.10	20.0	
			4	0.50	9.07	
			5	0.30	5.45	

Claims

- 25 1. A process for the purification of an industrial gas stream of hydrogen, carbon monoxide, air, nitrogen, oxygen, helium, argon, mono-olefins having from two to five carbon atoms per molecule, diolefins having four or five carbon atoms per molecule, paraffins, or acetylenes, by the removal of trace amounts of impurities therein, of one or more of water, hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide, hydrogen chloride, hydrogen cyanide, nitric acid, and mercaptans which
- 30 comprises contacting the said gas, at a temperature between 15 and 100°C, with a liquid essentially non-aqueous solution comprising from 0.5 to 15 weight percent of alkali or alkaline earth metal, in a liquid aliphatic polyhydric alcohol having a carbon to oxygen ratio of one to five, and at least two oxygens thereof being separated by not more than two sequential carbon atoms.
- 35 2. A process in accordance with claim 1, wherein the gas stream contains dissolved water vapour in an amount up to its limit of saturation therein, the water vapor being concurrently removed from the gas stream with other of such impurities.
3. A process in accordance with claim 1, wherein the concentration of the alkali metal is from 1 to 10 weight percent.
- 40 4. A process in accordance with claim 1, wherein the alkali or alkaline earth metal is sodium or potassium provided as the hydroxide.
5. A process in accordance with claim 4, wherein the alkali metal hydroxide is sodium hydroxide.
6. A process in accordance with claim 1, wherein the alkali metal or alkaline earth metal is potassium provided as the hydroxide or carbonate.
- 45 7. A process in accordance with claim 1, wherein the selected gas is ethylene.
8. A process in accordance with claim 1, wherein the selected polyhydric alcohol is triethylene glycol.
9. A process in accordance with claim 1, wherein the stream is continuously fed to a liquid body of the solution, the gas stream is removed from contact with the body into an atmosphere contiguous with the body in which the partial pressure of water vapor therein is insufficient significantly to increase
- 50 the water concentration in the stream.
10. A process in accordance with claim 9, wherein the water concentration in the stream leaving the body and the atmosphere is less than that contained in the stream fed to the body.
11. A process in accordance with claim 10, wherein the alkali and alkaline earth metal is potassium provided as a carbonate.
- 55 12. A process in accordance with claim 1, wherein the solution is regenerated periodically by thermal treatment.
13. A process in accordance with claim 12, wherein the thermal treatment is heating to a temperature to from 180 to 200°C.
- 60 14. A process in accordance with claim 1, wherein the contacting involves countercurrently passing the stream through the solution.

Patentansprüche

1. Verfahren zur Reinigung eines industriellen Gasstromes von Wasserstoff, Kohlenmonoxid, Luft,
- 65 Stickstoff, Sauerstoff, Helium, Argon Monoolefinen mit 2 bis 5 Kohlenstoffatomen pro Molekül,



Diölefinen mit 4 oder 5 Kohlenstoffatomen pro Molekül, Paraffinen oder Acetylenen durch Entfernung von Spuren Mengen von darin vorhandenen Verunreinigungen, und zwar einer oder mehrerer der folgenden: Wasser, Schwefelwasserstoff, Kohlendioxid, Carbonylsulfid, Schwefeldioxid, Chlorwasserstoff, Cyanwasserstoff, Salpetersäure und Mercaptane, welches die Merkmale umfaßt, daß man das Gas bei einer Temperatur zwischen 15 und 100°C mit einer flüssigen, praktisch nicht-wässrigen Lösung, in Berührung bringt, die 0,5 bis 15 Gew.-% Alkali- oder Erdalkalimetall in einem flüssigen aliphatischen mehrwertigen Alkohol mit einem Kohlenstoff: Sauerstoff-Verhältnis von 1 zu 5, wobei mindestens zwei Sauerstoffatome desselben durch nicht mehr als zwei aufeinanderfolgende Kohlenstoffatome getrennt sind, umfaßt.

2. Verfahren nach Anspruch 1, in welchem der Gasstrom gelösten Wasserdampf in einer Menge bis zu dessen Sättigungsgrenzwert enthält, wobei der Wasserdampf gleichzeitig mit anderen derartigen Verunreinigungen von dem Gasstrom entfernt wird.

3. Verfahren nach Anspruch 1, in welchem die Konzentration des Alkalimetalls 1 bis 10 Gew.-% beträgt.

4. Verfahren nach Anspruch 1, in welchem das Alkali- oder Erdalkalimetall Natrium oder Kalium zugeführt als Hydroxid ist.

5. Verfahren nach Anspruch 4, in welchem das Alkalimetallhydroxid Natriumhydroxid ist.

6. Verfahren nach Anspruch 1, in welchem das Alkalimetall oder Erdalkalimetall Kalium zugeführt als Hydroxid oder Carbonat ist.

7. Verfahren nach Anspruch 1, in welchem das gewählte Gas Ethylen ist.

8. Verfahren nach Anspruch 1, in welchem der gewählte mehrwertige Alkohol Triethylenglykol ist.

9. Verfahren nach Anspruch 1, in welchem der Strom kontinuierlich zu einer Flüssigkeitsmasse der Lösung zugeführt wird und der Gasstrom nach dem Kontakt mit der Flüssigkeit in eine an die Flüssigkeit angrenzende Atmosphäre entfernt wird, in welcher der Teildruck des Wasserdampfes nicht ausreicht, um die Wasserkonzentration im Strom wesentlich zu erhöhen.

10. Verfahren nach Anspruch 9, in welchem die Wasserkonzentration in dem die Flüssigkeitsmasse und die Atmosphäre verlassenden Strom geringer ist als diejenige, die in dem zur Flüssigkeit geführten Strom enthalten ist.

11. Verfahren nach Anspruch 10, in welchem das Alkali und Erdalkalimetall Kalium zugeführt als Carbonat ist.

12. Verfahren nach Anspruch 1, in welchem die Lösung periodisch durch thermische Behandlung regeneriert wird.

13. Verfahren nach Anspruch 12, in welchem die thermische Behandlung in einem Erhitzen auf eine Temperatur von 180 bis 200°C besteht.

14. Verfahren nach Anspruch 1, in welchem bei dem Inberührungbringen der Strom in Gegenstrom durch die Lösung geleitet wird.

Revendications

1. Procédé de purification d'un courant gazeux industriel d'hydrogène, d'oxyde de carbone, d'air, d'azote, d'oxygène, d'hélium, d'argon, de mono-oléfines ayant 2 à 5 atomes de carbone par molécule, de dioléfines ayant 4 ou 5 atomes de carbone par molécule, de paraffines ou d'hydrocarbures acétyléniques par élimination de traces d'impuretés qui s'y trouvent, formées d'un ou plusieurs composés tels que l'eau, le sulfure d'hydrogène, l'anhydride carbonique, le sulfure de carbone, l'anhydride sulfureux, le chlorure d'hydrogène, le cyanure d'hydrogène, l'acide nitrique et des mercaptans, qui consiste à faire entrer ledit gaz, à une température comprise entre 15 et 100°C, en contact avec une solution liquide essentiellement non aqueuse comprenant 0,5 à 15% en poids de métal alcalin ou alcalino-terreux dans un alcool polyhydroxylique aliphatique liquide ayant un rapport du carbone à l'oxygène de 1 à 5, et dont au moins deux atomes d'oxygène ne sont pas séparés par plus de deux atomes consécutifs de carbone.

2. Procédé suivant la revendication 1, dans lequel le courant gazeux contient de la vapeur d'eau dissoute en une quantité allant jusqu'à sa limite de saturation dans le courant, la vapeur d'eau étant éliminée du courant gazeux en même temps que certaines des autres impuretés.

3. Procédé suivant la revendication 1, dans lequel la concentration du métal alcalin va de 1 à 10% en poids.

4. Procédé suivant la revendication 1, dans lequel le métal alcalin ou alcalino-terreux est le sodium ou le potassium introduit sous la forme de l'hydroxyde.

5. Procédé suivant la revendication 4, dans lequel l'hydroxyde de métal alcalin est l'hydroxyde de sodium.

6. Procédé suivant la revendication 1, dans lequel le métal alcalin ou alcalino-terreux est le potassium introduit sous la forme de l'hydroxyde ou du carbonate.

7. Procédé suivant la revendication 1, dans lequel le gaz choisi est l'éthylène.

8. Procédé suivant la revendication 1, dans lequel l'alcool polyhydroxylique choisi est le triéthylèneglycol.



9. Procédé suivant la revendication 1, dans lequel le courant est chargé en continu dans une masse liquide de la solution, le courant gazeux est enlevé du contact avec la masse liquide et introduit dans une atmosphère contiguë à ladite masse dans laquelle la pression partielle de vapeur d'eau est insuffisante pour élever notablement la concentration en eau du courant.

5 10. Procédé suivant la revendication 9, dans lequel la concentration en eau du courant cessant d'être en contact avec la masse et avec l'atmosphère est inférieure à celle que renferme le courant arrivant au contact de la masse liquide.

11. Procédé suivant la revendication 10, dans lequel le métal alcalin ou alcalino-terreux est le potassium introduit sous la forme d'un carbonate.

10 12. Procédé suivant la revendication 1, dans lequel la solution est régénérée périodiquement par un traitement thermique.

13. Procédé suivant la revendication 12, dans lequel le traitement thermique consiste en un chauffage à une température de 180 à 200°C.

15 14. Procédé suivant la revendication 1, dans lequel le contact implique le passage à contre-courant de courant à travers la solution.

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