May 27, 1952 K. M. BROWN ET AL 2,598,034

DESULFLURIZATION OF HYDROCARBON GASES

Filed Jan. 19, 1949

FIG.1.

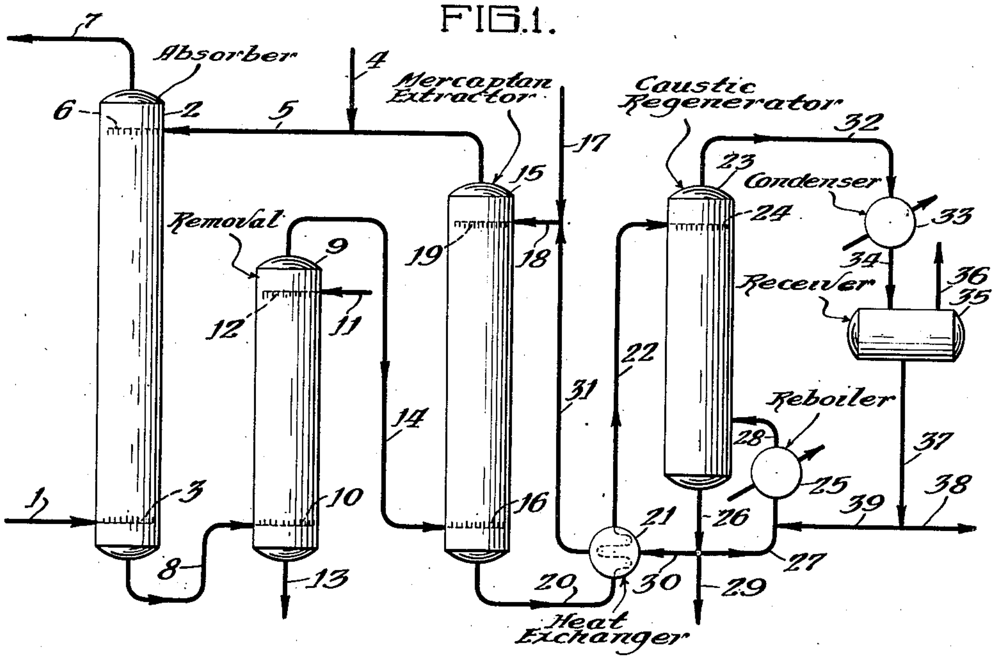
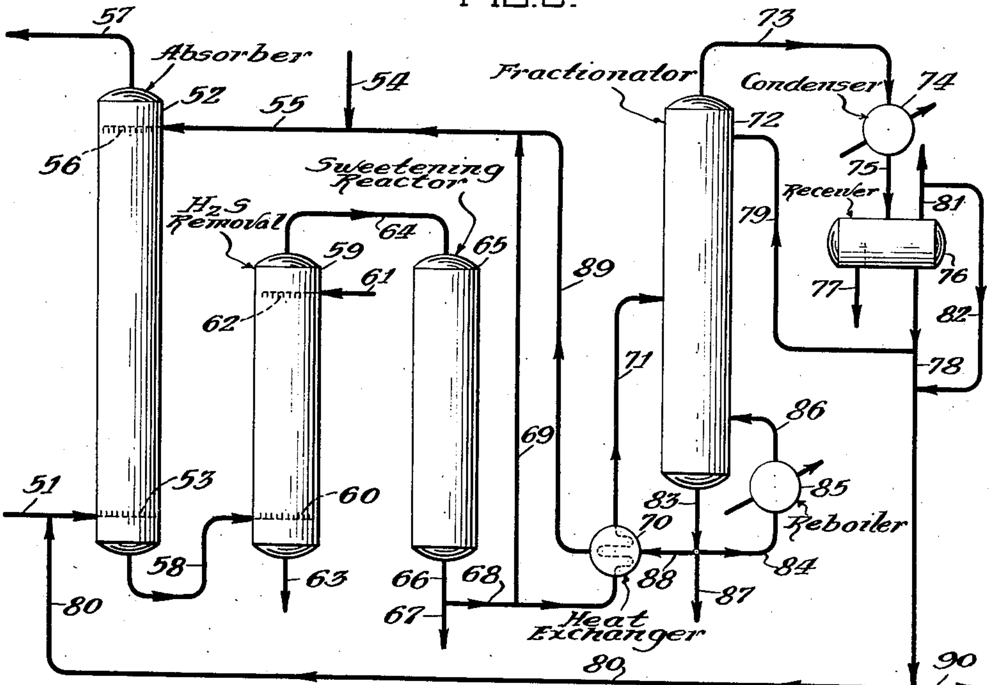


FIG.2.



Inventors:
Kenneth M. Brown
Clarence G. Gerhold
By: M. P. Venema
Bernard S. Kramer
Attorneys

Patented May 27, 1952

2,598,034

UNITED STATES PATENT OFFICE

2,598,034

DESULFURIZATION OF HYDROCARBON GASES

Kenneth M. Brown, Hinsdale, and Clarence G. Gerhold, Riverside, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application January 19, 1949, Serial No. 71,658

4 Claims. (Cl. 260—676)

The present invention relates to the desulfurization of hydrocarbons and more particularly to the removal of mercaptans by a novel process which minimizes the introduction of water into the hydrocarbon stream.

In many cases it is desired to remove mercaptans from a hydrocarbon stream without at the same time introducing water into the hydrocarbon stream and this is particularly true in the case of gases which are transported and handled under high pressures. For example, natural gas is usually given a dehydration treatment at the gathering point in a gas producing oil field, the extent of dehydration being controlled to meet a specified dew point. The dew point is predetermined at slightly above the lowest temperature which will be encountered in the transportation and handling of the gas. While some of the mercaptans are removed from the gas during the dehydration treatment, the remtaining mercaptan content is in many cases too high for satisfactory use. However, in removing the mercaptans subsequent to dehydration, care must be observed to preclude the introduction of water vapor into the gas stream because of the possible formation of solid hydrates due to reaction between the water and hydrocarbons. For this reason, the removal of mercaptans from dehydrated gas by conventional processes cannot be employed because of the fact that such processes are carried out n the presence of water, some of which would become entrained in said gas and thereby raise the dew point to such an extent that solid hydrate formation could take place. The present invention is directed to a novel method of removing mercaptans without at the same time undergoing the objection of increasing the moisture content.

In a broad embodiment the present invention relates to a process for desulfurizing a hydrocarbon stream containing mercaptan which comprises contacting said stream with a water immiscible solvent to extract mercaptan from said stream, separating a desulfurized hydrocarbon stream from solvent containing mercaptan, treating said solvent to reduce its mercaptan content, and recycling at least a portion of the solvent of reduced mercaptan content for further use within the process.

In a specific embodiment the present invention relates to a process for desulfurizing natural gas containing mercaptan which comprises contacting said natural gas with a liquid hydrocarbon solvent to extract mercaptan from said natural gas, separating desulfurized natural gas from hydrocarbon solvent containing mercaptan, treating said hydrocarbon solvent to remove mercaptan, and recycling at least a portion of the hydrocarbon solvent for further use within the process.

The novelty and utility of the present invention is illustrated further in the accompanying diagrammatic flow drawings which illustrate specific embodiments of the invention. In the interest of simplicity the following description of the drawings will be limited to the treatment of a hydrocarbon gas. Further, in the interest of simplicity, valves, pumps, compressors, mixers and the like have been omitted from the drawings.

Referring to Figure I, a hydrocarbon gas containing mercaptans is introduced to the process through line **1** and is directed into absorber **2**, preferably through a suitable spray arrangement as illustrated at **3**. In absorber **2**, the hydrocarbon gas is passed countercurrently to a suitable solvent introduced through line **4** and directed through line **5** to absorber **2**, preferably through a suitable spray arrangement as illustrated at **6**. In absorber **2**, all or at least a substantial portion of the mercaptans contained in the hydrocarbon gas stream will be transferred from the gas phase to the solvent liquid phase and thereby removed from the hydrocarbon gas. Similarly, all or a substantial portion of hydrogen sulfide, carbon dioxide or the like contained in the hydrocarbon gas will be transferred to the solvent phase and thereby removed from the hydrocarbon gas.

In the case here illustrated, absorber **2** comprises a single vertical vessel, which preferably contains suitable contacting means such as bubble trays, bubble decks, side to side pans, etc. and may or may not contain suitable packing material such as carbon Raschig rings, glass particles, excelsior, etc. It is understood that two or more absorption zones may be employed and also that mixing and settling zones may be used within the scope of the present invention.

Any suitable solvent which is water immiscible and in which mercaptans are preferentially soluble may be used within the scope of the present invention. A particularly suitable solvent comprises a liquid hydrocarbon fraction and thus may comprise a pentane, hexane, heptane, or octane fraction, aromatics such as benzene, toluene, xylene, etc., higher boiling hydrocarbons, or mixtures thereof. In another embodiment of the invention, the solvent may comprise high boiling alcohols, high boiling ketones, etc. which are substantially water immiscible. In still another embodiment of the invention the solvent may comprise disulfides, either formed within the process as will hereinafter be described in connection with one embodiment of the invention or introduced from an extraneous source.

The hydrocarbon gas is withdrawn from absorber **2** through line **7** and will contain less mercaptans than contained in the original gas stream charged to the process. The solvent containing mercaptans, hydrogen sulfide and carbon dioxide, etc. when present is withdrawn from absorber **2** through line **8** and is introduced to H_2S removal zone **9**, preferably through a suitable spray arrangement as illustrated at **10**. Any suitable method of removing hydrogen sulfide and carbon dioxide, etc. when present from the solvent may be employed. One particularly suitable method is the non-regenerative caustic process in which caustic is introduced to zone **9** through line **11**, preferably through a suitable spray arrangement, as illustrated at **12**. In view of the fact that the caustic cannot be economically regenerated, usually a low Baumé caustic of the order of 5 to 15° Baumé is used in this step of the process. Hydrogen sulfide, carbon dioxide, etc. will be absorbed in the caustic and removed from the lower portion of zone **9** through line **13**, while the solvent, substantially free of hydrogen sulfide, carbon dioxide, etc. is withdrawn from the upper portion of zone **9** through line **14**. Other suitable methods of removing hydrogen sulfide include the use of alkanol amines and particularly diethanol amine, tripotassium phosphate, etc., and it is understood that zone **9** will comprise suitable equipment both for the absorption or removal of the hydrogen sulfide and for regeneration of the particular reagent used. When the gas stream is substantially free of hydrogen sulfide, zone **9** may be omitted and the solvent may be supplied from zone **2** direct to zone **15**.

The solvent withdrawn through line **14** from zone **9** will be substantially free of hydrogen sulfide, carbon dioxide, etc. but will contain mercaptans and, in accordance with the present invention, is introduced by way of line **14** to mercaptan extractor **15**, preferably through a suitable spray arrangement as illustrated at **16**. In zone **16** the solvent is passed countercurrently to caustic introduced through lines **17** and **18** to zone **15**, preferably through a suitable spray arrangement as illustrated at **19**. The caustic is preferably of 10° to 25° Baumé. It is understood that any suitable alkaline reagent which will remove mercaptans from the solvent may be employed within the scope of the present invention and that the alkaline reagent may include various promoters to increase solubility of the mercaptans in the alkaline reagent. Suitable promoters include methanol, phenols, cresols, potassium isobutyrate, etc. In place of a single vertical absorption zone as illustrated in the drawing, it is understood that two or more such zones, or mixing and settling zones may be employed. Likewise, zone **15** preferably contains suitable packing material such as carbon Raschig rings and/or contacting means such as bubble trays, bubble decks, side to side pans, etc.

The solvent substantially free of mercaptans is withdrawn from the upper portion of zone **15** through line **5** and is returned to absorber **6** for further use within the process. The caustic containing mercaptans in the form of sodium mercaptides is withdrawn from the lower portion of zone **15** through line **20** and is directed through heat exchanger **21** and line **22** to caustic regenerator **23**, preferably through a suitable spray arrangement as illustrated at **24**. In zone **23** the caustic is regenerated by hydrolysis and stripping to convert the sodium mercaptides to caustic and mercaptans. In the case here illustrated heat is supplied to the lower portion of regenerator **23** by means of reboiler **25**. It is understood that any other suitable means of heating the lower portion of zone **23**, such as by direct introduction of steam, etc. may be employed. The regenerated caustic is withdrawn from the lower portion of zone **23** through line **26** and a portion thereof is recycled by way of line **27** through reboiler **25** and line **28** back to zone **23**. While the remaining portion may be withdrawn from the process through line **29** preferably at least a portion thereof is recycled by way of line **30**, heat exchanger **21** and lines **31** and **18** back to extractor **15** for further use within the process.

Mercaptans and water evaporated in zone **23** are removed from the upper portion thereof through line **32** and are directed through condenser **33** and line **34** into receiver **35**. Mercaptans separate from water in receiver **35**, the mercaptans are withdrawn from the process through line **36**, and the water is withdrawn through line **37**. While all or a portion of the water may be removed from the process through line **38**, at least a portion thereof is recycled by way of lines **39** and **27** through reboiler **25** and line **28** to regenerator **23** to serve as a hydrolyzing medium therein.

Figure II of the drawing illustrates another specific embodiment of the invention. In this embodiment the mercaptans are converted into disulfides, and the disulfides are subsequently separated from the solvent and removed from the process. Referring to Figure II, absorber **52**, lines **51**, **54**, **55**, **57** and **58** and spray arrangements **53** and **56** correspond to absorber **2** and the similar lines and spray arrangements illustrated in Figure I of the drawing. Similarly H_2S removal zone **59**, lines **61** and **63** and **64** and spray arrangements **60** and **62** correspond to H_2S removal zone **9** and similar lines and spray arrangements as illustrated in Figure I. The description hereinbefore set forth in connection with Figure I applies to zones **52** and **59** of Figure II. The solvent substantially free of hydrogen sulfide, carbon dioxide, etc. but containing mercaptans is directed by way of line **64** into sweetening reactor **65**. Any suitable sweetening system may be used in this step of the process, a particularly suitable sweetening system comprising the use of copper chloride either as a fixed bed or slurry type of operation. It is understood that any other suitable system in which the mercaptans are converted to disulfides may be employed within the scope of the present invention. It is also understood that zone **65** will include suitable means for regenerating the treating reagent.

The effluent product from reactor **65**, comprising solvent containing disulfides is withdrawn from the lower portion of zone **65** through line **66** and, while a portion thereof may be removed from the process through line **67**, at least a portion thereof is directed through line **68** and may be recycled by way of lines **69** and **55** to zone **52** for further use in the process. As hereinbefore set forth, the presence of disulfides is not objectionable and, in one embodiment of the invention, the solvent itself may comprise a disulfide fraction. In another embodiment of the invention, the solvent containing disulfides is directed by way of line **68** through heat exchanger **70** and line **71** to fractionator **72**. In fractionator **72** the disulfides are distilled overhead and removed from zone **72** through line **73** and are passed through condenser **74** and line **75** into receiver **76**. Water produced during the sweetening reaction or otherwise introduced in the process is separated in receiver **76** from disulfides. The water is withdrawn from the process through line **77** and the disulfides are withdrawn from receiver **76** through line **78**. A portion of the disulfides may be recycled by way of line **79** to the upper portion of fractionator **72** to serve as a cooling and refluxing medium therein. The disulfides may also contain gas dissolved from the gas stream by the solvent, and may be subjected to distillation and stabilization for recovery of such gas by well known means not illustrated. The gas dissolved from the gas stream by the solvent which appears as a gas phase in receiver **76** may be recycled to absorption zone **52** by means of lines **81**, **82**, **78**, **80** and **51**. When desired, all or a portion of the disulfides may be withdrawn from the process through line **90**.

The solvent reduced in disulfides is withdrawn from the lower portion of fractionator **72** by way of line **83**, a portion thereof is recycled by way of line **84**, reboiler **85** and line **86** to fractionator **72**, while the remaining portion may be removed from the process through line **87** but preferably is recycled at least in part through line **88**, heat exchanger **70** and lines **89** and **55** to absorber **52** for further use within the process.

As a further precaution to insure that the moisture content of the hydrocarbon gas stream will not be increased, it is within the scope of the present invention to include, when desired, a dehydration step for the recycled solvent being returned by way of line **5** in Figure I or by way of lines **69** or **89** in Figure II or the fraction being recycled from receiver **76** by way of line **80** as also illustrated in Figure II. The amount of these streams will be considerably smaller than the hydrocarbon gas stream charged to the process. Any suitable dehydration system may be employed including the use of liquids such as diethylene glycol, glycerine, zinc chloride, calcium chloride, etc. or solid materials such as calcium chloride, calcium oxide, silica gel, activated alumina, charcoal, magnesium oxide, etc.

In place of the alkaline reagent as desecribed in connection with Figure I or the copper sweetening as described in connection with Figure II of the drawings for the removal of mercaptans, it is understood that any other suitable system for removing mercaptans from the solvent may be employed within the scope of the present invention. Other suitable but not necessarily equivalent processes for removal or conversion of mercaptans include the well known doctor process, hypochlorite treating, the use of hydrogen fluoride, etc. It is understood that the necessary absorption, mixing, settling and regenerating zones will be provided to suit the particular process employed. These processes are well known and do not require detailed description in the present specification.

It is thus seen that the novel process of the present invention offers a method of removing mercaptans from hydrocarbon gas streams without at the same time increasing the moisture content thereof.

We claim as our invention:

1. A process for desulfurizing a hydrocarbon gas stream containing mercaptan which comprises contacting said gas stream with a liquid hydrocarbon solvent to extract mercaptan from said gas stream, separating a desulfurized gas stream from hydrocarbon solvent containing mercaptan, treating said hydrocarbon solvent with copper chloride to convert mercaptan to disulfide, and supplying at least a portion of the hydrocarbon solvent containing disulfide to the aforesaid contacting step.

2. The process of claim 1 further characterized in that the hydrocarbon gas stream also contains hydrogen sulfide, the hydrocarbon solvent extracts the hydrogen sulfide along with the mercaptan, the hydrocarbon solvent containing mercaptan and hydrogen sulfide is treated to remove hydrogen sulfide prior to treating with copper chloride to convert mercaptan to disulfide.

3. A process for desulfurizing a hydrocarbon gas stream containing mercaptan which comprises contacting said gas stream with a liquid hydrocarbon solvent to extract mercaptan from said gas stream, separating a desulfurized gas stream from hydrocarbon solvent containing mercaptan, subjecting the separated solvent to a sweetening treatment to convert mercaptan to disulfide, and supplying at least a portion of the disulfide-containing solvent to the aforesaid contacting step.

4. A process for desulfurizing a hydrocarbon gas stream containing mercaptan which comprises contacting said gas stream with a mercaptan solvent comprising disulfides, separating the resultant mercaptan-containing solvent from the desulfurized gas, converting the mercaptans in the solvent to disulfides, and supplying at least a portion of the latter to the aforesaid contacting step.

KENNETH M. BROWN.
CLARENCE G. GERHOLD.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,785,365	Seil	Dec. 16, 1930
1,796,621	Ramage	Mar. 17, 1931
1,935,725	Perl	Nov. 21, 1933
1,986,228	Seguy	Jan. 1, 1935
2,041,364	Miller	May 19, 1936
2,146,353	Rosenbaugh	Feb. 7, 1939
2,269,467	McCullough	Jan. 13, 1942
2,297,650	Frey et al.	Sept. 29, 1942
2,297,751	Dryer et al.	Oct. 6, 1942
2,311,342	Kerns	Feb. 16, 1943
2,312,820	Henderson	Mar. 2, 1943
2,383,416	Reed	Aug. 21, 1945
2,395,509	Shaw	Feb. 26, 1946
2,411,105	Nixon et al.	Nov. 12, 1946
2,434,868	Sample et al.	Jan. 20, 1948