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WASHING LIQUID FOR LOW TEMPERATURE APPARATUS, PARTICULARLY GAS LIQUEFACTION AND FRACTIONATING APPARATUS

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1 Claim. (Cl. 252—158)

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This invention relates to improvements in washing liquids for low temperature apparatus.

Countercurrent heat exchangers, washing columns, separating columns and fractionating apparatus are used for the liquefaction and fractionation of gas mixtures. In these known apparatuses, the gas constituents which have been isolated in liquid or gas form remove the heat from the gases which are to be processed. It is in this manner that air and coke oven gas are liquefied to a large extent and split into their individual constituents. Even with good preliminary purification, the entering gases still contain quantities of gaseous impurities such as carbon dioxide, nitrogen oxide, acetylene, etc. These impurities solidify at the low temperatures present, i. e. temperatures as low as —180° C. and therefore deposit on the heat exchange surfaces.

If these deposits were allowed to remain, they would clog the apparatus. In order to avoid this clogging these deposits must be removed from time to time. This removal may be accomplished by thawing the liquefaction and fractionating apparatus. The thawing procedure, however, entails great danger in that if acetylene or nitrogen oxides have deposited in solid form on the heat exchange surfaces during the operation, explosions may occur. Due to the ever present danger of these explosions, it is preferable not to use the thawing procedure. Accordingly, it is preferable to wash the heat exchange and separating apparatuses with solvents which have a low solidification point, and also dissolve chemicals such as caustic soda. By use of these chemicals, the solidified gas constituent can be rendered harmless by neutralization or other reaction.

It is advantageous to introduce these solvents into the apparatus at a low temperature so that there is no unfavorable heat exchange in the apparatus when the solvents are added. A solution containing 90% by volume of methanol and 10% by volume of sodium hydroxide solution, the sodium hydroxide solution containing 7% by weight of NaOH (70–80 grams NaOH in 1000 cc. of this solution), has been used in the past. Mixtures of ethyl alcohol and sodium hydroxide solution or potassium hydroxide solution have also been used for this purpose.

The solidification point of the mixture consisting of 90% by volume of methanol, 10% by volume of sodium hydroxide solution of the above mentioned concentration is approximately between —110 and —115° C. The heat exchanges and separating apparatus assume temperatures of about —150° C. and even lower upon splitting up of the coke oven gas. When washing this apparatus in cold condition with the said mixture of 90% by volume of methanol and 10% by volume of sodium hydroxide solution the danger that the solvent will partially solidify in the apparatus and that the solidified gas constituents cannot be completely removed is always present. If this occurs, a new washing becomes necessary after a very short period of operation. In accordance with the invention, we have found a new washing liquid which overcomes these difficulties. According to the present invention, a washing solution consisting of an alcoholic alkali solution which contains hydrocarbons of a low boiling point, is used. We have found that it is preferable to use a mixture of approximately 90% by volume of methanol and 10% by volume of dilute sodium hydroxide solution, said solution containing about 7% by weight NaOH, which has been previously saturated with low boiling hydrocarbons and preferably with hydrocarbons with a molecular size of less than 5 carbon atoms. This new mixture has a pour point of —145° C., so that when it is used as a washing solvent it no longer solidifies or becomes viscous within the low temperature apparatus which is being washed out. The washing liquid in accordance with the invention may, for example, be used as follows.

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Coke oven gas at a temperature of —40° C. are cooled in 2 counter-current apparatuses by returning gases to a temperature of —150° C. Upon cooling, the ethylene in the gases is separated as a liquid. The separated ethylene is in part subjected to a decreased pressure and in part cooled to still a lower temperature in a special counterflow apparatus with liquid nitrogen. The gas mixture from which the ethylene has been removed then flows through another counter-current heat-exchange after which it is rectified in an evaporator having a washing column connecting to it.

After a relatively long period of operation, all the heat-exchanging apparatuses (countercurrent apparatuses) contain a thin layer of solidified gas constituents. In order to remove these deposits the apparatuses are filled, without prior thawing, with the new washing liquid in accordance with the invention. With this new washing liquid there is now no danger that local solidification or thickening of this liquid

will prevent its further penetration to all parts of the apparatus.

It can thus be seen that one great advantage among others in using the new washing liquid in accordance with the present invention consists in the fact that the separating apparatus treated is capable of operation for a considerably longer period of time than before, for instance, up to 2,000 hours of operation. Before the use of the new washing liquid, washing had to be effected in general after about 1000 hours of operation.

The liquid, in accordance with the invention, is not limited to the washing or purifying gas liquefaction and fractionation installations but may be used anywhere where a mixture of alcohol and alkali solution with a low pour point is desired. With an increase in the content of the aqueous alkali solution, and in particular sodium hydroxide solutions, the pour points of the alcoholic alkali solution is considerably increased.

The addition of the hydrocarbon considerably lowers the pour point, for example, a mixture containing 90% by volume of ethyl alcohol and 10% by volume of potassium hydroxide solution (7% by weight KOH) solidifies at —130° C. If this mixture is saturated with gaseous hydrocarbons, as for example methane, ethane, propane or the corresponding olefins or mixtures thereof, the pour-point drops to —145° C. so that such an alcoholic potassium hydroxide solution can be used at considerably lower temperatures than where heretofore possible.

Similar reactions also apply to propyl alcohol. A mixture of 90% isopropyl alcohol and 10% sodium hydroxide solutions of 7% concentration solidifies at —105° C. After saturation with "gasol" i. e. hydrocarbons containing 3 and 4 carbon atoms in the molecule, the pour-point is lowered to —120° C.

Also other aliphatic alcohols containing 1 to 3 carbon atoms in the molecule may be used instead of methyl alcohol. The aqueous alkali lye may thus be mixed, for example, also with ethyl alcohol or propyl alcohol. Among the propyl alcohols, the ordinary propyl alcohol may most preferably be used; also isobutyl alcohol is in part still suited as alcoholic component.

The alkali concentration of the aqueous constituents of the solvent in accordance with the invention should not be so high that solid hydrates of the alkali hydroxides form when cooling down to for instance —120° C. Therefore, the concentration of the aqueous alkali hydroxide solutions should generally not be in excess of 10% of alkali hydroxide.

In order to lower the solidification point of the alcoholic alkali lye, paraffinic or olefinic hydrocarbons containing 1 to 4 carbon atoms in the molecule may be used. Methane, ethane, ethylene, propane, propylene, butane, and butylene may thus be employed for the method in accordance with the invention. A hydrocarbon mixture which may be separated, for instance, from coke oven gas and which is known in the market as "gasol" is very well suited. It contains on an average 19% propane, 45% propylene, 5% ethane, 2% ethylene, 3% butane, 13% butylene, and 13% by volume of other constituents (N_2, O_2, CO_2, CH_4).

A solution which consists of 90% by volume of methanol and 10% by volume of an aqueous sodium hydroxide solution containing 7% by weight of NaOH absorbs per volume approximately 400 to 500 cc. of this hydrocarbon mixture at a temperature of approximately 18° C.

It can now be seen from the above that the invention lies in composition of a new washing liquid containing an alcohol, an alkali solution, and low boiling hydrocarbons.

We claim:

Washing liquid for low-temperature apparatus comprising a mixture of about 90% of an alcohol selected from the group consisting of methanol and ethanol, and about 10% of an aqueous alkali solution of about 7% concentration of a member selected from the group consisting of potassium hydroxide and sodium hydroxide substantially saturated with a normally gaseous hydrocarbon having between 1 and 4 carbon atoms in its molecule.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,445,064	Hall et al.	July 13, 1948

FOREIGN PATENTS

Number	Country	Date
161,568	Switzerland	July 1, 1933