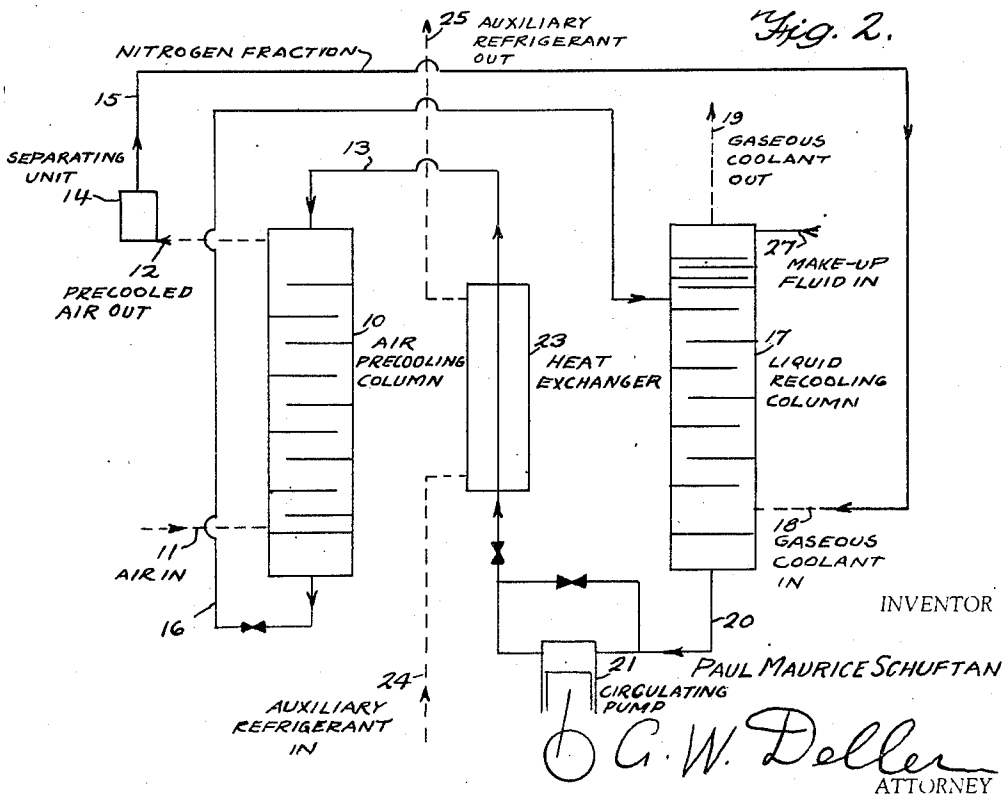
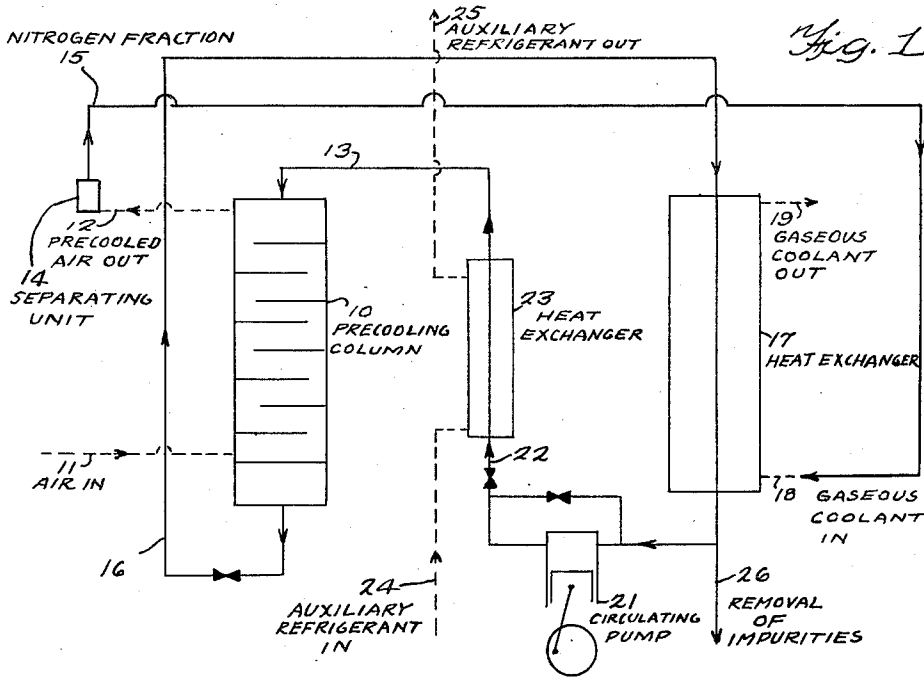


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P. M. SCHUFTAN
PRECOOLING AND PURIFICATION OF GASEOUS
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PRECooling AND PURIFICATION OF GASEOUS MIXTURES PRIOR TO LIQUEFACTION

Paul Maurice Schüfftan, Richmond Hill, England,
 assignor to The British Oxygen Company Limited,
 London, England, a British Company

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The present invention relates to the precooling and purification of gaseous mixtures prior to liquefaction.

In what follows the word "impurities" must be understood to embrace also an impurity in the singular.

The term "precooling" properly refers to the precooling of the gaseous mixture by means of an auxiliary refrigerant, whereby the overall thermodynamic efficiency of a liquefaction cycle employing Joule-Thompson expansion is much improved. In practice, however the term "precooling" conveniently refers to the whole of the cooling of the gas performed before it proceeds to the liquefaction unit proper, which usually includes also some cooling obtained from one or more of the cold gaseous products from the sequent liquefaction process. Precooling in this sense is therefore usually performed in two steps, but may of course in principle be performed solely by means of an auxiliary refrigerant or solely by means of cold gaseous products of the sequent liquefaction process.

In the whole precooling process as above described the temperature of the gaseous mixture is reduced to the point at which the vapour pressure of impurities of relatively high vapour pressure and relatively high freezing point is reduced sufficiently to ensure prolonged operation of the liquefaction unit proper before its construction by solid deposits of these impurities. Examples of impurities of the type referred to are water in air, and benzene and/or naphthalene in carbonisation gases. Constituents not originally present in the gaseous mixture, such as oil vapours from a compressor lubricant, which would also obstruct the liquefaction unit, and in an air separation unit might cause a danger of explosion, will also be removed to a considerable extent in the precooling process.

Precooling as carried out hitherto has suffered from several disadvantages. In normal practice a gaseous mixture is precooled by bringing it into direct heat exchange through the walls of a thermal conductor with gaseous products from the sequent liquefaction process and/or with an auxiliary refrigerant. Owing to the deposition of impurities in the solid state, the precoolers become obstructed in a relatively short time and are therefore usually provided in duplicate so that one unit may be thawed out whilst the other unit is performing its function as a cooler. In view of the necessity of securing a reasonable time of operation before complete obstruction of the gas passages, it is necessary for these pas-

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sages to be of relatively large cross-sectional area and the heat transfer coefficient from the gas to the walls of the passages then becomes low. The exchangers, therefore, either have to be very large and expensive, or relatively large heat exchange losses resulting in a high power consumption for the auxiliary refrigerating cycle have to be tolerated.

Another disadvantage is the discontinuity in the operation of the plant occasioned by periodically switching over the exchangers. Such discontinuity results in temperature and pressure fluctuations throughout the plant, which, apart from being undesirable in themselves, cause a larger amount of the impurities with relatively high vapour pressure and relatively high freezing point to reach the separation unit than would be the case if the temperatures and pressures remained steady.

A further disadvantage is the necessity of providing several changeover valves which are prone to leakage. The leakage of even a small amount of warm gas through a valve in the closed position into a gas stream which has been precooled causes formation of very finely-divided solid particles which may be carried far into the liquefaction unit and cause early obstructions therein.

It is an object of this invention to ensure a continuous precooling operation in a simple device in which pressure losses and cold losses are both uniformly low whereby a saving in power consumption together with improved steadiness and ease of operation may be achieved.

According to this invention there is provided a method of precooling a gaseous mixture having an impurity content of relatively high vapour pressure and relatively high freezing point as a preliminary to liquefying at least a part of the mixture wherein the precooling is effected by contacting the mixture in counter-current flow with a cold liquid medium of low freezing point adapted to cool the gas mixture and to retain such a proportion of the impurity content that the vapour pressure of the residual impurities in the cooled gaseous mixture is so low as to ensure extended operation of the plant in which the sequent liquefaction is effected. Depending upon the nature of the impurities to be removed and the temperature, the mass transfer may involve solution in the liquid medium, or liquefaction and the formation of an emulsion in the liquid medium, or solidification and the formation of a suspension of solid particles in the liquid medium of the impurities. Usually, however, one impurity will predominate (e. g. water vapour in air) and in such a case the

liquid medium will be chosen so as to dissolve this impurity. It is an advantage of this invention that the vapour pressure of a soluble impurity will be reduced by the presence of the liquid medium, quite apart from the effect of the low temperature.

The contacting of the gaseous mixture with the cold liquid medium may be effected in any suitable contacting device such as a scrubber or a packed or plate column. The liquid medium at the required low temperature is introduced at or near the top of the device and as it travels down the column in counter-current to the upwardly flowing gas stream, both heat- and mass-transfer from the gaseous mixture to the liquid medium occur. As a result of the heat transfer, under efficient operating conditions the liquid will leave the contacting device at a temperature only slightly below the inlet temperature of the gaseous mixture.

After contacting the gaseous mixture, the liquid medium may be recooled for re-use and prior to re-use may be subjected to a purification treatment for a reduction of the impurity content. Where the impurities are in solution they may be removed by distillation, crystallisation or solvent extraction; where they are in the immiscible liquid state they may be removed by decantation, and where they are in the solid state they may be removed by filtration.

Where one or more gaseous products is or are available from the sequent liquefaction, such gaseous product or products or part thereof (hereinafter termed "the gaseous coolant," which term is intended to cover both gaseous products which are to be conserved as valuable products of the liquefaction process and those which are to be rejected as waste products) may be used to re-cool the liquid medium, additional cold being supplied if necessary from an auxiliary refrigerating cycle. The liquid medium may, for instance, be recooled by bringing it into indirect heat exchange with the gaseous coolant through the wall of a thermal conductor.

Alternatively, the liquid medium may be recooled by direct counter-current contact with the gaseous coolant, additional cold being supplied if necessary from an auxiliary refrigerating cycle. When such direct contact recooling is adopted it is of advantage to retain in the liquid medium up to the stage when it is contacted with the gaseous coolant at least a part of those impurities having a vapour pressure higher than that of any other constituent or constituents of the liquid medium whereby the cooling produced by heat transfer between the gaseous coolant and the liquid medium is augmented by cold produced by mass transfer of impurity to the gaseous coolant.

Where the impurity to be removed is a substance which is present as an initial constituent of the liquid medium and has a vapour pressure higher than that of the other constituent or constituents of the liquid medium, additional cold may be produced by contacting the liquid medium with a volume of the gaseous coolant exceeding that required to vaporise that amount of the substance which was removed as impurity from the gaseous mixture, the liquid medium being restored to its original composition by adding thereto a quantity of the substance equal to the excess evaporated.

The direct contact of the gaseous coolant with the liquid medium is of particular advantage in those cases where the vaporisation of the impurity into the gaseous coolant is not objection-

able (as, for instance, when the impurity is of no value and when there is no objection to contamination of the gaseous coolant by it), for firstly the necessity for a separate apparatus to remove the impurity from the liquid medium is avoided and secondly additional cooling of the liquid medium is produced by the evaporation of the impurity. This will result in a reduction in the cold production required and therefore in the power consumption of the plant. For instance, in an air separation process where water vapour is an impurity to be removed and a glycol-water solution is used as the liquid medium, the latter may be at least partly recooled by bringing it into counter-current contact with the nitrogen fraction as the gaseous coolant whereby an appreciable amount of extra cooling of the liquid medium will normally be obtained as a result of water evaporation into the nitrogen stream. This extra cooling will reduce the power consumption of the separation plant or alternatively that of the auxiliary refrigeration cycle if such is used to provide final recooling of the liquid medium.

Where the amount of the substance evaporated from the liquid medium exceeds that removed as impurity from the gaseous mixture, it is necessary, as stated above, to add to the liquid medium a quantity of the substance equal to the excess evaporated so as to restore the liquid medium to its original composition. The addition may conveniently be made by bringing the substance to be added into intimate contact with the effluent gaseous coolant so as to strip therefrom any valuable component of the liquid medium which may have been vaporised by the gaseous product. For instance, when a glycol-water solution is used as the liquid medium to remove water vapour from compressed air, the water added to compensate for the excess evaporated over that removed from the compressed air can be used to strip glycol vapour from the emerging gaseous coolant.

The choice of the liquid medium will depend on the precooling temperature to be achieved and on the nature of the impurities to be removed from the gaseous mixture and will also be influenced by particular conditions obtaining in the plant under consideration. Depending on the nature of the impurities to be removed, liquid media which could be used are, for example, hydrocarbons, glycerol and other polyhydric alcohols, both aliphatic and aromatic, monohydric alcohols, acetones, aldehydes, organic acids, or liquids of low freezing point composed of inorganic and/or organic substances dissolved in water.

In order to avoid excessive losses of valuable substances contained in such liquid media, it will be of advantage to use ingredients having the lowest possible vapour pressure compatible with the low freezing point of the liquid.

In the specific case of the precooling of air prior to liquefaction and separation into a nitrogen fraction and an oxygen-fraction where water vapour is present in the air as an impurity liable to choke the liquefaction and separation units, the liquid medium may be a glycol-water solution. When using the eutectic composition containing about 58% by weight of glycol and 42% by weight of water, it is possible to obtain precooling temperatures approaching minus 49° C. At such low temperatures the vapour pressure of the residual water content in the air emerging from the pre-cooler will be so low that the liquefaction and separating units may operate for prolonged periods before having to be

thawed out on account of choking with ice. The water taken up from the air by the glycol/water mixture may be removed by any known means, such as revaporisation or crystallisation, so as to enable the liquid medium to be re-used. It will be of particular advantage to use for this purpose one of the products of separation, the nitrogen fraction or the oxygen fraction, both of which are substantially dry and available at low temperature, so that cooling and water removal are effected simultaneously as already explained in more general terms.

The invention will now be described in further detail with reference to the accompanying drawing, which shows diagrammatically in Figure 1 one form of apparatus suitable for use in carrying out the invention, employing indirect recooling of the precooling liquid; and Figure 2 shows diagrammatically another form of apparatus employing direct recooling.

A compressed gaseous mixture to be precooled, and having an impurity content of relatively high vapour pressure and relatively high freezing point, is led from a compressor (not shown) to the bottom of a counter-current contact unit 10 through an inlet pipe 11. The contact unit 10 may comprise a packed column or a plate column or other suitable contact device. The air passes upwardly through the unit 10 in counter-current contact with a descending stream of precooling fluid consisting of a glycol-water solution, and the purified air leaves the top of the contact unit through outlet pipe 12 and passes to a separating unit 14 in which the nitrogen fraction is separated and passed through pipe 15 for use as a gaseous coolant.

The precooling liquid enters the top of the unit 10 through pipe 13, and after absorbing the impurities from the gaseous mixture being treated, passes from the bottom of the unit 10 through pipe 16 to the top of a heat exchanger 17, in which it is brought into heat exchange relationship with the gaseous products of separation entering the exchanger 17 through pipe 15 and pipe 18 and leaving through pipe 19. From the exchanger 17, the precooling fluid is led through pipe 20 to a circulating pump 21 and thence through pipe 22 to a second heat exchanger 23, where it is passed in indirect heat exchange with an auxiliary refrigerant which enters exchanger 23 through pipe 24 and leaves it through pipe 25. From the exchanger 23, the re-cooled fluid is conveyed through pipe 13 to the top of the contact unit 10.

The heat exchanger 17 may be of the type in which heat transfer takes place through the wall of a thermal conductor, for example, it may be a tubular heat exchanger, as shown in Figure 1; in this case water vapor condensed from the glycol-water solution during its passage through the exchanger 17 is removed through a drain pipe 26. It may on the other hand be a direct contact heat exchanger or scrubber similar to the unit 10, as shown in Figure 2. In the latter case, the volume of gaseous coolant passing through the exchanger 17 may be so great as to remove more water from the glycol-water solution than the latter has absorbed from the air. The glycol-water solution is in this case restored to its original composition by the addition of make-up water. Make-up water is supplied as indicated at 27 in Figure 2.

I claim:

1. The method of precooling air containing water vapour as a preliminary to liquefying at

least part of the air and separating therefrom a nitrogen fraction, said method comprising bringing the air into direct contact and in counter-current flow with a glycol-water solution at a temperature below 0° C. adapted to cool the air and to retain such a proportion of the water content that the partial vapour pressure of any residual water in the cooled air is so low as to ensure extended operation of the plant in which the sequent liquefaction is effected, and restoring the glycol-water solution to a condition suitable for re-use by a regeneration process which comprises bringing it into direct contact with a gaseous coolant derived from the sequent liquefaction in order simultaneously partially to re-cool the glycol-water solution and to reduce the water content thereof, additional cold being supplied to the glycol-water solution to complete the re-cooling thereof from an auxiliary refrigerating cycle.

2. The method of precooling air containing water vapour as a preliminary to liquefying at least part of the air and separating therefrom a nitrogen fraction, said method comprising bringing the air into direct contact and in counter current flow with a glycol-water solution at a temperature below 0° C. adapted to cool the air and to retain such a proportion of the water content that the partial vapour pressure of any residual water in the cooled air is so low as to ensure extended operation of the plant in which the sequent liquefaction is effected, and restoring the glycol-water solution to a condition suitable for re-use by a regeneration process which comprises bringing it into direct contact with a gaseous coolant derived from the sequent liquefaction in order simultaneously to re-cool the glycol-water solution and to reduce the water content thereof, the volume of gaseous coolant being such that the water removed during the regeneration process exceeds that absorbed by the glycol-water solution and restoring the glycol-water solution to its original composition by adding water thereto.

3. The method of precooling air containing water vapour as preliminary to liquefying at least part of the air and separating therefrom a nitrogen fraction, said method comprising bringing the air into direct contact and in counter current flow with a glycol-water solution at a temperature below 0° C. adapted to cool the air and to retain such a proportion of the water content that the partial vapour pressure of any residual water in the cooled air is so low as to ensure extended operation of the plant in which the sequent liquefaction is effected, and restoring the glycol-water solution to a condition suitable for re-use by a regeneration process which comprises bringing it into direct contact with a gaseous coolant derived from the sequent liquefaction in order simultaneously to re-cool the glycol-water solution and to reduce the water content thereof, the volume of gaseous coolant being such that the water removed during the regeneration process exceeds that absorbed by the glycol-water solution, and restoring the glycol-water solution to its original composition by adding water thereto, the added water being brought into intimate contact with the effluent gaseous coolant so as to strip therefrom and return to the glycol-water solution any glycol entrained by the gaseous coolant.

4. The method of precooling air containing water vapour as a preliminary to liquefying at least part of the air and separating therefrom

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a nitrogen fraction, said method comprising bringing the air into direct contact and in counter current flow with a glycol-water solution at a temperature below 0° C. adapted to cool the air and to retain such a proportion of the water content that the partial vapour pressure of any residual water in the cooled air is so low as to ensure extended operation of the plant in which the sequent liquefaction is effected, and restoring the glycol-water solution to a condition suitable for re-use by a regeneration process which comprises re-cooling the glycol-water solution with its augmented water content by bringing into direct contact therewith the separated nitrogen fraction in a volume exceeding that required to vapourise from the glycol-water solution that quantity of water which was removed from the air by the original glycol-water solution, and restoring the glycol-water solution to its original composition by adding thereto an amount of water equal to the excess evaporated by said nitrogen fraction, said added water being brought into intimate contact with the effluent

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nitrogen fraction so as to strip therefrom any glycol entrained therein.

PAUL MAURICE SCHUFTAN.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,501,415	Lafferty	July 15, 1924
1,724,513	Pollitzer	Aug. 13, 1929
1,791,086	Sperr	Feb. 3, 1931
2,093,805	De Baufre	Sept. 21, 1937
2,134,699	Brewster	Nov. 1, 1938
2,141,997	Linde et al.	Dec. 27, 1938
2,198,142	Wade	Apr. 23, 1940
2,214,678	Raigorodsky	Sept. 10, 1940
2,245,028	Farris	June 10, 1941
2,288,461	Keith et al.	June 30, 1942

FOREIGN PATENTS

Number	Country	Date
591,095	France	June 27, 1925