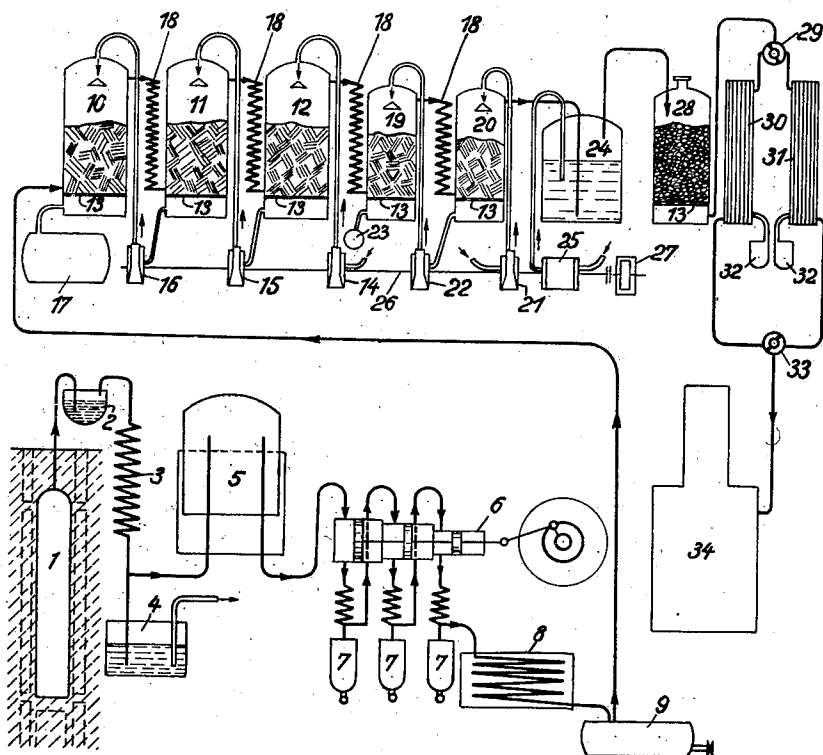


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 PROCESS FOR THE SEPARATION OF CONSTITUENTS
 OF COKE OVEN GASES AND THE LIKE
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PROCESS FOR THE SEPARATION OF CONSTITUENTS OF COKE-OVEN GASES AND THE LIKE

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In the extraction of by-products from coke oven gases, as now practised, the proceeding is such that the coke oven gases, on leaving the ovens, are allowed to cool to the ordinary temperature of the air. During that time, 5 tar vapors and water vapors are separated, which vapors contain in solution also a part of the ammonia. The coke oven gases are thereupon washed with water for the purpose 10 of removing the greatest part of the ammonia, and then with the so-called middle oils or washing oils, the greatest part of the benzole being washed out. Sometimes the coke oven gases thus treated, are further 15 freed from their sulphuretted hydrogen by a wet or dry process.

In the treatment of coke oven gases by compression and cooling to a low temperature for the purpose of obtaining pure hydrogen or mixtures of hydrogen and nitrogen, it has been found that the present by-product extraction is insufficient in a two-fold respect.

The present removal of the benzole is insufficient, and the remaining traces of benzole are easily liable to obstruct the separation apparatus at low temperatures.

It has also been found that in addition to these so-called by-products, it is further 30 necessary to remove various other secondary constituents if the gas mixture separation apparatus is to work properly.

The chief among these secondary constituents is in the first place carbonic acid, further 35 various sulphur-cyanogen- and other nitrogen compounds, and finally acetylene and its homologues.

Although as a rule coke oven gases contain acetylene and some of the other secondary constituents only in very small quantities (mostly under 0.1%), the said acetylene and other constituents are liable to cause considerable trouble unless they be first removed as completely as possible.

45 The process according to this invention consists substantially in the removal of the said by-products and secondary constituents being effected by means of ammonia and by means of acetone with the simultaneous use 50 of pressure and cold.

It is true that it has been already proposed to remove the carbonic acid from distillation gases by treatment with ammoniacal liquor. The old methods of working took place, however, in an unsatisfactory manner as the carbonic acid was not sufficiently washed out. 55

As has been shown by researches this disadvantage must be attributed to the fact that the ammoniacal liquor used was not sufficiently concentrated, and that for the complete removal of the carbonic acid the gases must show a considerable vapor tension of the ammonia. 60

As regards the use of acetone and of similarly acting organic solvents with low freezing point (for instance methylene-dimethylether, ethylide-diethylether, ethyl-acetate), it is already known, it is true, that such solvents absorb large quantities of acetylene. It is however a new discovery that these solvents absorb acetylene also from gases which contain less than 0.1% acetylene, at a pressure of say 10 atmospheres and at a temperature of minus 60° C. in such a complete manner that the coke oven gas thus treated 75 shows less than 0.0001% acetylene. This percentage can no longer be considered as injurious, and besides it can be reduced again to about one hundredth by cooling to minus 90° C. 80

The fact that according to the invention the coke oven gases have to be compressed for the purpose of extracting the by-products, does not involve any extra expenditure, as coke oven gases are anyhow compressed already (mostly to 10 to 30 atmospheres) for the purpose of subsequent separation of the coke oven gases into their single constituents. For the same reason, the use of cold in the present case also does not involve any considerable extra expenditure, as the coke oven gases have in any case to be strongly cooled subsequently and this to a temperature of minus 90° C. and preferably still lower. 90

The whole operation benefits moreover by the fact that ammonia in its aqueous solutions has a very low freezing point. 95

The practical carrying out of the process according to the invention is illustrated in the accompanying drawing. 100

The distillation gas escaping from the coke oven 1 passes into the tar receiver 2. The gas is thereupon cooled in the cooler 3 to about the air temperature, the condensing tar and water vapors collecting in the tank 4. The gas is conveyed to the gas tank 5 from which it is drawn by a multi-stage compressor 6. In passing from one compressor stage to another, the gas may be cooled, the condensates—more particularly naphthaline and anthracene—collecting in separators 7. The compressed gas is then cooled further in the cooler 8, the benzol being separated in a practically complete manner and collecting in the tank 9. The gas passes through the washing towers 10, 11, 12. These washing towers are provided with a grate 13 and may be filled with Raschig rings and the like which rest on the grate 13. The washing tower 12 is supplied by the pump 14 with ammonia which, after passing through the tower 12, is conveyed by means of the circulating pump 15 to the tower 11, and thence, by means of the circulating pump 16, to the tower 10. The ammoniacal liquid charged with carbonic acid, sulphur, cyanogen and partly also with the remaining benzole, passes into the tank 17 from which it is taken for further treatment.

It has been found advisable to treat coke oven gases rich in carbonic acid, with less cold ammonia, and coke oven gases poor in carbonic acid, with very cold ammonia. This can be easily carried out by placing in circuit energetically acting gas coolers 18 at the passage of the coke oven gases from the tower 10 into the tower 11 and from the latter into the tower 12.

The gas then passes into the washing towers 19 and 20 in which it is washed with acetone. Fresh acetone is supplied by the feed pump 21 to the washing tower 20 from which the acetone washing liquid is brought by the circulating pump 22 into the washing tower 19. These washing towers 19 and 20 may also be provided with grates 13 and with filling of Raschig rings. The acetone liquid charged with acetylene and other injurious secondary constituents, passes into the collector tank 23 in order to be conveyed from it to the regenerating apparatus.

If necessary, the gas is then passed through the boiler 24 in which the gas is washed with any desired acid of low freezing point. The acid is supplied to the tank 24 by the feed pump 25. The feed and circulating pumps mentioned, may be driven singly or in groups or as shown in the drawing by means of a joint shaft 26 with a joint motor 27. The gas then passes into the tank 28 which is filled with strongly absorbent substances, such as for instance active charcoal, silica gel, soda lime, in order to keep back as far as possible the vapors of the washing liquids utilized. Through the distributor valve 29 the gas is

then cooled to a very low temperature by means of one of the coolers 30 or 31 connected together in parallel and the liquids which are condensed during that process, collect in separators 32.

With the distributing valves 29 and 33 in the position shown in the drawing, the gas flows through the cooler 31. The coke oven gas thus cooled for instance down to minus 90° then passes into the gas separation apparatus 34 where it is decomposed into the single constituents or groups of constituents.

The method of working illustrated in the drawing is a purely continuous one until the admission into the distributor valve 29, and only the coolers 30 and 31 are intermittently worked. There is no reason why the washing with ammonia and acetone should not also be carried out intermittently by the arrangement of towers connected together in parallel. This would be done chiefly when, owing to the gas speeds which are to be used, or owing to the coke oven gases containing a high percentage of secondary constituents to be washed out, the separations taking place during the washing out, are so great as to make the apparatus liable to become choked.

The cooling of the coke oven gases, which is required in this method of working, may be effected partly by means of cold aqueous salt brine (for instance in the case of condensation of benzol, in the cooler 8) or by evaporating the ammonia (for instance as in the coolers 18), or by means of very cold gas fractions escaping from the gas separation apparatus 34, as is for instance the case for the coolers 30 and 31.

Concentrated ammoniacal liquor, for instance with 25 or 50% ammonia, or also liquefied ammonia gas, may be used for this washing process.

Although the process described in the foregoing may be varied in many ways, the method of working illustrated in the above drawing, in which the gases during their travel come in contact at constantly lower temperature with always fresh ammonia washing liquor, appears to be particularly advantageous.

This method of working makes possible a more complete saturation (neutralization of the washing liquid), as the fresh, still relatively warm, coke oven gases, on meeting the already strongly saturated or neutralized ammoniacal liquor, have a certain tendency to expel the free ammonia into the next much colder washing towers. The fact that the coke oven gases pass the last place in contact with pure ammonia, ensures that the percentage of carbonic acid, sulphur and cyanogen compounds in the coke oven gases becomes approximately equal to zero.

In order to prevent the ammonium salts which are partly precipitated in that process and which, are sometimes also mixed with

benzole snow, from forming strongly adhering crusts, it is advisable to add to the washing liquid small quantities of some substances which volatilize with difficulty or are oily or slimy, such as for instance paraffin oil, but care must be taken that these additions should have approximately the same specific gravity as that of the washing liquid.

As a rule some ammonia is left in the acetone liquid. This is not injurious as they can be easily separated from each other by treating the liquid for instance with some suitable acid (for instance sulphuric acid, nitric acid, phosphoric acid), the ammonia being converted into the corresponding salts, and the acetone being left behind.

If it is desired to free the coke oven gases completely from ammonia and acetone vapors before their admission into the decomposition apparatus, they are caused to pass further through a washing tower which is charged with acid solutions of low freezing point, and thereupon through a tank which is filled with soda lime, active charcoal or silica gel.

The hereinbefore described sequence of treatment with ammonia and acetone (solvents) need not be absolutely adhered to. Thus for instance the coke oven gas may be first compressed, thereupon washed with acetone and with ammonia, and only then can be effected the strong preliminary cooling for instance to -60 or -90°C ., so that the vapors of these washing agents are separated.

As is well known, acetone mixes with ammonia within wide temperature limits, and in certain conditions the washing with ammonia may be combined with acetone washing. In any case it is in practice not a disadvantage if during the working acetone is separated in the ammoniacal liquor, or ammonia in the acetone liquid.

As already stated, the lower homologue of acetylene and other secondary constituents which easily resinify are also washed out by the organic solvents (such as acetone, for instance) at the same time as the acetylene.

Finally it must be mentioned that with the same process may be freed completely other gases also, these gases containing similar secondary constituents, such as for instance splitting, cracking and low temperature carbonization gases, from their secondary constituents in the manner here described.

The condensates such as anthracene, naphthalene and benzoles collecting in this process of working in the single separators are purified or separated from one another in the usual manner.

The ammonia washing liquid which has taken up the greatest part of the remaining secondary constituents, may either be treated directly with acid, such as for instance hydrochloric acid, sulphuric acid, nitric acid,

phosphoric acid, for the purpose of converting the ammonia into stable ammonium salts, or it is heated to a sufficient extent (for instance to $80-100^{\circ}\text{C}$.) the ammonia dissociating from the salts formed in the washing liquid (ammonium carbonate, carbamate, sulphide, cyanide) and being conveyed through the acid saturators.

If the ammoniacal washing liquor is heated with the above mentioned salts under pressure, they are converted for the most part into urea or thio-urea.

Even when working with a mixture of ammonia and acetone or other solvents, the consumed washing liquid may be treated cold or hot with one of the above mentioned acids, in which case both free ammonia and the ammonia which was bound, are converted into more stable ammonium salts, and practically pure acetone is left behind.

The acetone (or other solvent) charged with acetylene is caused to expand, after leaving the washing towers, in separate vessels (23) and, if necessary, distilled over in order thus to free it from the absorbed gases.

What we claim is:—

1. In a process for the treatment of gas mixtures which contain hydrogen, hydrocarbons and carbon oxides, more particularly of coke oven gases, by compression and cooling to a low temperature below -100°C ., the step of submitting the gas mixture before its cooling to a low temperature, to a preliminary treatment consisting in washing the same with ammonia and an acetylene solvent of organic nature and of a low freezing point, the preliminary treatment being effected at a temperature which is not so low than that of the final treatment.

2. A process according to claim 1, wherein the preliminary treatment of the gas consists in washing with ammonia in concentrated form and with an acetylene solvent of organic nature, both washing liquids having a low freezing point.

3. A process according to claim 1, wherein the preliminary treatment of the gas consists in washing with liquefied ammonia gas and with an acetylene solvent of organic nature having a low freezing point.

4. A process according to claim 1, wherein the preliminary treatment of the gas consists in washing with ammonia and with acetone.

5. A process according to claim 1, wherein the preliminary treatment of the gas mixture is effected in two stages by washing the gas at first with the one and thereafter with the other of the two washing media.

6. A process according to claim 1, wherein the gas mixture is treated in a first stage with ammonia and thereafter in a second stage with the acetylene solvent.

7. A process according to claim 1 wherein the preparatory washing of the gases is fol-

lowed by cooling the gas mixture in successive stages at first to a temperature above -100° C. adapted to effect condensation of the vapors of the washing liquids but not sufficient for final separation of the gas mixture constituents and thereafter in a further stage to a temperature below -100° C. for final separation of the gas mixture constituents.

8. A process according to claim 1 wherein the gas mixture after having been washed with ammonia and acetylene solvent is treated with reagents adapted to remove the washing agents therefrom.

In testimony whereof we have signed our names to this specification.

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