Patented July 16, 1935

2,008,253

UNITED STATES PATENT OFFICE

2,008,253

PROCESS OF SEPARATING HYDROCYANIC ACID

Walter Klempt, Dortmund-Eving, Germany, assignor to Gesellschaft für Kohlentechnik Mit Beschränkter Haftung, Dortmund-Eving, Germany

No Drawing. Application May 11, 1932, Serial No. 610,747. In Germany May 29, 1931

7 Claims. (Cl. 23—76)

This invention relates to an improved process of separating hydrocyanic acid from such industrial gases which, like lighting gas, coke oven gas, and the like, contain, besides hydrocyanic acid, also sulphuretted hydrogen and ammonia.

The hydrocyanic acid has up to now been removed from said gases by washing these latter with an aqueous suspension of finely distributed free sulphur, but that process necessitates the employment of very finely ground sulphur of a foreign origin, at least free sulphur, which first must be produced by means of a particular method.

I have discovered that the employment of specially manufactured sulphur for the purpose of removing hydrocyanic acid from gases can be dispensed with if, in order to convert this acid into ammonium-sulphocyanate, the sulphuretted hydrogen itself contained in the respective gases is used. If sulphide of nickel or another suitable nickel salt by which sulphide of nickel is precipitated owing to the action of the ammonia and the sulphuretted hydrogen, is admixed to the washing liquid, free sulphur is disengaged from the sulphide of nickel under the oxidizing influence of the oxygen likewise contained in the respective gases, but the thus formed hydroxide of nickel is at once again converted into sulphide of nickel by the further supply of sulphuretted hydrogen whereby again sulphur is separated, and so on. The thus formed free sulphur reacts with the sulphide of ammonia contained in the liquid whereby ammonium poly-sulphide is formed which takes up the hydrocyanic acid contained in the gases whereby ammonium-sulphocyanate is formed. If there is more ammonium-polysulphide than is requisite to take up the hydrocyanic acid, the excess thereof is oxidized to ammonium-thiosulphate which contaminates the rhodammonium lye formed and renders the working of the same difficult.

The behaviour of the substances mentioned can, however, be influenced in such a manner that exclusively thiocyanate is formed if the amount of the nickel salt admixed to the washing liquid is accommodated to the contents of oxygen in the respective gas about as follows: With consideration of the usual contents of oxygen of from 0.5 to 0.7 percent by volume for instance in coke oven gases the contents of nickel in the washing liquid should not be materially higher than from 0.5 to 1 gram of nickel per 1 liter of the washing liquid, if the separation of more sulphur than is requisite for the formation of ammonium-thiocyanate and, thus, also the formation of ammonium-thiosulphate, shall be prevented. On the other hand, if the gas contains from 2 to 2.5 percent by volume of oxygen, the contents of nickel in the washing liquid should not be materially higher than from 0.1 to 0.3 gram per 1 liter, if complete removal of the hydrocyanic acid shall be achieved without the disadvantage of the formation of an undesired excess of sulphur.

When carrying out the process according to the present invention, it is suited to the purpose to use a little less nickel than is requisite for obtaining quantitative removal of the hydrocyanic acid. One is then sure that no soluble sulphur compounds, especially ammonium-thiosulphate, arise in the solution. The rest of the hydrocyanic acid still contained in the gases can be reliably removed from them by adding a slight amount of finely pulverized sulphur to the washing liquid.

In order to make matters still more clear I point out what follows: The present invention relates to the practically complete removal of hydrocyanic acid from coal distillation gases, but my improved process does not aim also at the complete removal of the sulphuretted hydrogen also contained in the respective gases. Owing thereto, only so much sulphuretted hydrogen is removed from the gases as is requisite to convert the cyanogen radical, —CN, into thiocyanogen radical, —CNS. The excess of the sulphuretted hydrogen is removed by another way which does not form a part of the present invention.

In carrying out my improved process, I make use of such an amount of nickel that only a part of the sulphuretted hydrogen is washed out in the form of sulphide of nickel, and another part thereof forms sulphide of ammonia with the ammonia present in the gas. This sulphide of ammonia forms, together with the sulphur separated by the sulphide of nickel by the slight amount of the oxygen contained in the gases, ammonium-polysulphide, which gives off its sulphur to the hydrocyanic acid contained in the gases, forming therewith ammonium-thiocyanate, as already stated. Thus, the larger the amount of nickel contained in the washing liquid, the larger is also the amount of free sulphur which the oxygen contained in the coke oven gas can separate, the sulphur reacting with the existing ammonium-sulphide and forming poly-sulphide. There is thus, under this condition, more poly-sulphide formed than is requisite for converting the cyanogen radical, —CN, into thiocyanogen radical, —CNS, so that now the oxygen of the gases has an opportunity to oxidize the excess of ammonium-polysulphide to ammonium-thiosulphate. If the amount of nickel contained in the

washing lye is fixed already from the beginning, then the same disadvantage will be experienced if from any reason during the service the content of oxygen in the coke oven gases increases. If, for instance, at a certain definite contents of hydrocyanic acid and simultaneously therewith at a content of oxygen of 0.4% by volume a content of 0.05% by volume of nickel in the washing liquid has been found to be proper for forming only so much poly-sulphide as is requisite for converting the hydrocyanic acid into thiohydrocyanic acid, then that content of nickel is no longer suited for the purpose in view if the content of oxygen in the gases amounts to more than 0.4% by volume. In this case the excess of ammonium-polysulphide formed is in the position to form, besides ammonium-thiocyanate, also ammonium-thiosulphate, and this be the more the case, the more the content of oxygen in the gas increases.

The effect of my improved process will now be shown with the aid of the following examples:

A coke oven gas subjected to the washing operation was composed as follows:

From 10.5 to 11.5 g/cbm of H_2S
from 1 to 1.2 g/cbm of HCN
6 g/cbm of NH_3
2.1 g/cbm of CO_2
from 0.8 to 1.2 g/cbm of O_2.

Every hour 2 cbm of this gas were washed in a small iron vessel filled with grid-work. The washing lye was set in circulation by means of a cog-wheel pump with a speed of about from 6 to 8 liters per hour and was distributed over the grid-work by means of a spray. In three tests 1000 cm^3 of the washing liquid contained:

In the first case:
11.5 grams of NH_3 and 35 grams of S
In the second case:
11.5 grams of NH_3 and 2.5 grams of Ni in the form of $Ni(OH)_2$
In the third case:
11.5 grams of NH_3 and 0.75 gram of Ni in the form of $Ni(OH)_2$.

In the first case 35 grams of S were added after 20 cbm of gas had been led through said vessel. Computed relatively to the amount of sulphocyanate formed until the end of the test 10% of sulphur in excess had been employed.

The amount of hydrocyanic acid removed from the coke oven gas in all tests amounted in average to from 98.9% to 100% of the HCN contained in the gas so that only from 0 to 0.01 gram of this acid could be ascertained in the purified gas.

After 50 cbm of gas had been led through the washing liquid contained in said vessel, there were ascertained in the washing liquids:

In the first case:
14.9% of ammonium rhodanide (=53 g. of HCN) and 1.2% of thiosulphate.
In the second case:
15.2% of ammonium rhodanide (=54 g. of HCN) and 9.8% of thiosulphate.
In the third case:
14.7% of ammonium rhodanide (=52.2 g. of HCN) and 1.3% of thiosulphate.

While, thus, as regards the washing-out of hydrocyanic acid, the three tests showed no differences, great differences were found when the washing liquid was examined with respect to the undesired contents of thiosulphate. Considering the comparatively high percentage of oxygen in the gas very much thiosulphate is obtained when large amounts of nickel are employed. On the other hand, slight amounts of nickel in the washing liquid cause the formation of only so much sulphur as is requisite for the formation of rhodanium.

Further experiments were made with a coke oven gas containing only from 0.3 to 0.4% of oxygen. The content as regards the other components was practically the same as in the above-mentioned three cases, and the tests were carried out in the same manner.

In the fourth case the washing liquid contained 11.5 grams of Ni in the form of Ni(OH) in 1000 ccm. The hydrocyanic acid removed from the gas amounted to from 96 to 100% of the total amount contained in the raw gas. After 50 cbm. of gas had been led through the washing liquid, this latter contained 14.3% of ammonium-rhodanide (=50.7 grams of HCN) and 1.4% of ammonium-thiosulphate. This shows that if the percentage of oxygen in the gas is only small a percentage of the same magnitude as in the second of the three cases at first dealt with (2.5 grams of nickel in the form of $Ni(OH)_2$ in 1000 ccm.) causes only a slight formation of thiosulphate.

In the fifth case also a gas poor in oxygen was used. The percentage of nickel amounted only to 0.55 gram in 1 liter, also in the form of $Ni(OH)_2$, approximately corresponding to the third case. The washing liquid contained 11.5 grams of NH_3 and 0.55 gram of Ni in the form of $Ni(OH)_2$ in 1000 ccm. After 50 cbm. of gas had been led through the liquid this latter contained 10.4% of ammonium rhodanide (=37 grams of HCN) and 0.4% of thiosulphate. The washing-out of hydrocyanic acid amounted only to from 65 to 78%. It was found that the contents of 0.55 g. of nickel in 1 liter of liquid is not sufficient for the complete washing-out of the hydrocyanic acid if the percentage of the oxygen in the gas is so slight as stated. The formation of thiosulphate is in such a case, of course, particularly slight.

By adding such a small amount of elementary sulphur that it was just sufficient to bind that portion of hydrocyanic acid which had not been washed-out, complete washing-out of the hydrocyanic acid was attained also with a sixth test carried out in a manner analogous to the fifth case. As the amount of the nickel to be added cannot be computed prior to carrying out the test, in that it depends on a variety of circumstances, such as percentage of oxygen, of sulphuretted hydrogen, and of hydrocyanic acid in the gas, of the amount of the washing solution and of the gas to be led through it, as well as on the temperature, the process must be started in this way that one commences with the lowest addition of nickel to the washing liquid appearing admissible with respect to the percentage of oxygen of the gas, and that then the contents of nickel in the solution is slowly increased until about from 98 to 100% of the hydrocyanic acid are being washed out. It will then be found that at the same time only so much sulphur is washed out of the gas as is requisite for the conversion of the entire amount of hydrocyanic acid into rhodanium-hydrogen and that the formation of thiosulphate is without importance.

In the carrying out of my present improved process the oxygen contained in the gases acts upon the sulphide of nickel precipitated by the sulphuretted hydrogen in this way according to the equation

$$NiS+\tfrac{1}{2}O_2+H_2O=Ni(OH)+S,$$

that it is temporarily converted into nickel-hydroxide which, however, is instantaneously converted into sulphide of nickel by the sulphuretted hydrogen present, the nickel-hydroxide acting, as it were, catalytically for the oxidation of the sulphuretted hydrogen to disengage sulphur. In this way the percentage of the ammonium-sulphocyanide contained in the washing lye can, while the lye is circulating, be increased up to 35% without any decrease of the washing effect during the removal of the hydrocyanic acid.

I have also discovered that if the percentage of hydrocyanic acid in coking gases is very high or if the washing is carried out at an increased temperature, a part of the sulphide of nickel can be dissolved in the form of a nickel cyan complex salt. As this dissolved nickel cannot take part in the conversion of the hydrocyanic acid into thio-hydrocyanic acid, as above described, in that it is no more precipitated by the sulphuretted hydrogen, the degree of the washing-out decreases in such a case at once so that, in order to re-establish the proper proportion between the oxygen and the active nickel of the washing liquid fresh amounts of nickel in the form of sulphide of nickel or of a nickel compound adapted to be precipitated by sulphuretted hydrogen must be added for rendering the washing process again quantitative.

This method delivers, it is true, an ammonium-sulphocyanate of a satisfying concentration, suffers, however, from the drawback that it enriches in ineffective nickel complex salts whereby its further working is rendered difficult. If the re-obtainment of the nickel converted into the complex salt would be given up, the process would become expensive by reason of the requisite continual supply of fresh amounts of nickel.

Now, according to my improved process, the re-obtainment of the nickel in a form suited for the removal of the hydrocyanic acid is rendered possible thereby that parts of the solution which have been withdrawn during the service, or that the entire amount of the solution, after the readily concentrated ammonium-sulphocyanide solution has been removed, is stirred with sulphur prior to its being further worked. In this way there forms in the solution which contains ammonia, as well as sulphuretted hydrogen, ammonium-polysulphide which decomposes the complex nickel cyan compound into sulphocyan, there being precipitated black sulphide of nickel, and the cyan radical being converted into said sulphocyan. Such a decomposition of the nickel cyan complex salt can, I emphasize, be effected only by the ammonium-hydrosulphide of ammonia likewise present in the liquid. The sulphide of nickel separated in any suitable manner is re-conducted to the washing plant. This sulphide of nickel re-obtained from the solution presents the advantage over freshly precipitated sulphur that it can be dissolved in solutions treated with gases containing hydrocyanic acid only with pretty great difficulty, that is to say, soluble nickel cyan complex salts cannot easily be formed, but nevertheless transmission of the oxygen present in the coke oven gases to the sulphuretted hydrogen of the respective gases can be effected quickly and productively. The sulphide of nickel regenerated in that manner remains longer suited for the transmission of the sulphur to the hydrocyanic acid than does ordinary freshly precipitated sulphide of nickel.

If the ammonium-sulphocyanate solution, in the case of a too strong concentration as regards the sulphocyanate, should contain too little sulphide of ammonia to precipitate the nickel from out of the nickel cyan complex compound, and to effect the intermediate formation of polysulphide of ammonia, which may easily occur when operating at too high a temperature, for instance 30° C., with gases poor in NH_3 and H_2S it is a matter of course that sulphuretted hydrogen from any source, for instance in the form of raw condensed gas water, may be added to the liquor, or the waste vapors of the ammonia-water separators or waste damp of saturators may be introduced into the liquid. In order to furnish the ammonium polysulphide requisite for the decomposition of the nickel cyan complex salt one can also proceed in the manner that otherwise prepared ammonium polysulphide is added to the ammonium sulphocyanate lye which contains ammonium sulphide, instead of stirring sulphur into said lye. In this modification of the method the stirring phase may be dispensed with. Slight heating of the liquid is advantageous for increasing the decomposition of the nickel cyan complex salt.

Instead of decomposing the thus formed nickel cyan complex salts by treating them with sulphur, or with polysulphide respectively, in the manner described, this part of the process may be carried out also in this way that the formation of such nickel cyan complex salts during the washing procedure is prevented already from the beginning. It is suited to the purpose to effect that during the service by reducing the washing temperature. If, for instance, the coking gas is washed under normal conditions at a temperature of about 30° C., it is possible to increase the concentration of the sulphide of ammonia by diminishing the temperature to 20° C. In most cases this contrivance will already suffice to prevent the sulphide of nickel from being dissolved, that is to say to prevent the formation of soluble nickel cyan complex compounds which can no more be precipitated by means of sulphide of ammonium.

If the percentage of sulphuretted hydrogen contained in the gases to be dealt with is not too small, one will succeed when proceeding in the just stated manner by again precipitating already dissolved nickel from the nickel cyan complex in the form of sulphide of nickel as a complex salt, as sufficient ammonium-polysulphide is forming. There is, however, presupposed in this case that still sufficient sulphide of nickel is suspended in the washing liquid. A sufficient quantity of sulphide of nickel must be present at all events. If that is not the case, either the lacking amount of sulphide of nickel, or a nickel salt adapted to be precipitated by sulphide of ammonia, or ammonium polysulphide, or (to form this substance) elementary sulphur, must be added in order to start the reaction by the sulphide of nickel present.

Another method for the re-obtainment of the sulphide of nickel especially in the case that the coke oven gases or the like are poor in oxygen consists in treating the washing liquid with air prior to conducting it back into the washing vessel. The sulphide of nickel still present in the form of a suspension delivers in that case free sulphur which reacts with the existing sulphide of ammonia in forming ammonium-polysulphide, and so precipitates in the form of sulphide of nickel that part of the nickel which has been dis-

solved as a complex salt. The amount of air used to carry out this procedure must, however, be only slight as it is only to replace that portion which the gases are lacking. Treating the washing liquid with air takes place preferably in an intermediate vessel provided for the circulation of the liquid. It is also possible to design the pipe leading to the upper part of the washing vessel or tower in such a manner that the liquid is treated with air while it flows through said pipe.

I claim:

1. The process of separating hydrocyanic acid in the form of ammonium thio-cyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with the aid of washing lyes containing nickle compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure.

2. The process of separating hydrocyanic acid in the form of ammonium thiocyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with the aid of washing lyes containing nickel compounds, said process consisting in dissolving nickel cyanogen complex compounds, introducing ammonium polysulphide into the solution so as to precipitate thereby sulphide of nickel out of said solution of the nickel cyanogen complex compounds, and introducing into the washing lye already at the commencement of the washing operation an amount of said sulphide of nickel sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure.

3. The process of separating hydrocyanic acid in the form of ammonium thio-cyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with aid of washing lyes containing nickel compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure; introducing ammonium-polysulphide into the lye so as to precipitate the nickel contained in the same in the form of a dissolved nickel cyanogen complex salt, and finally, conducting the sulphide of nickel so obtained back into the washing process.

4. The process of separating hydrocyanic acid in the form of ammonium-thio-cyanate from gases containing said acid, ammonia and sulphuretted hydrogen with the aid, of washing lyes containing nickel compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure; introducing ammonium polysulphide into a part of the washing lye during the washing operation so as to precipitate the nickel contained in the same in the form of a dissolved nickel cyanogen complex salt, and finally, conducting the liquid containing suspended sulphide of nickel back into the washing process.

5. The process of separating hydrocyanic acid in the form of ammonium thio-cyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with the aid of washing lyes containing nickel compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure; introducing ammonium polysulphide into the entire amount of the washing lye and after the saturation of said lye with ammonium thiocyanate has become a maximum so as to precipitate the nickel contained in the same in the form of a dissolved nickel cyanogen complex salt, and finally, conducting the separated sulphide of nickel so obtained back into the washing process.

6. The process of separating hydrocyanic acid in the form of ammonium thio-cyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with the aid of washing lyes containing nickel compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, and insufficient to form soluble sulphur compounds rendering the lye impure, treating the liquid leaving the washing circuit and containing still suspended nickel sulphide and dissolved nickel cyanate complex salt with air so as to produce thereby the sulphur necessary for the formation of ammonium polysulphide to precipitate said nickel cyanogen complex salt in the form of sulphide of nickel, and conducting said liquid thereafter back into the washing process.

7. The process of separating hydrocyanic acid in the form of ammonium thio-cyanate from gases containing said acid, ammonia, and sulphuretted hydrogen with the aid of washing lyes containing nickel compounds, said process consisting in adding to the washing lye an amount of the nickel compounds sufficient to produce the amount of ammonium-polysulphide requisite for the conversion of the hydrocyanic acid into ammonium-thiocyanate, said addition of the nickel compounds being, besides, chosen so small that the hydrocyanic acid is not completely washed out, and adding, finally, pulverulent sulphur so as to render the further washing-out quantitative.

WALTER KLEMPT.