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P. J. HARINGHUIZEN
PROCESS FOR PREPARING HYDROGEN-NITROGEN
MIXTURES FROM COKE OVEN GAS

2,820,769

Filed April 6, 1956

2 Sheets-Sheet 1

FIG. 1

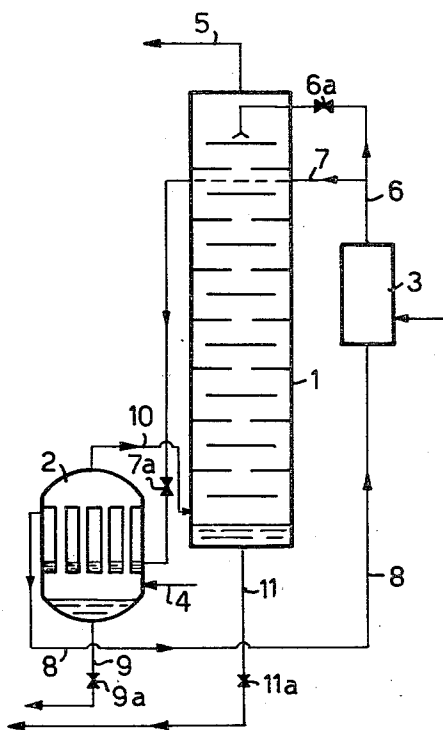
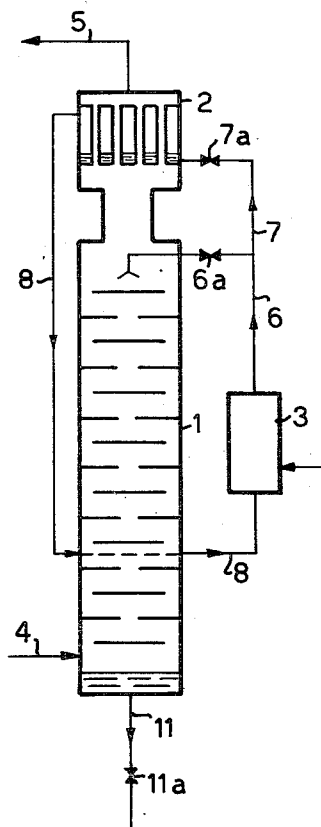


FIG. 2



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2 Sheets-Sheet 2

FIG.3

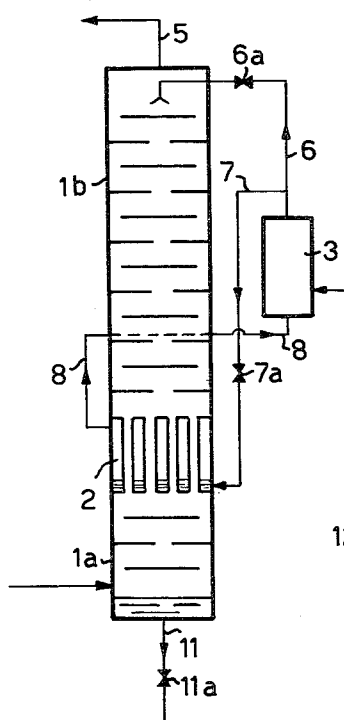
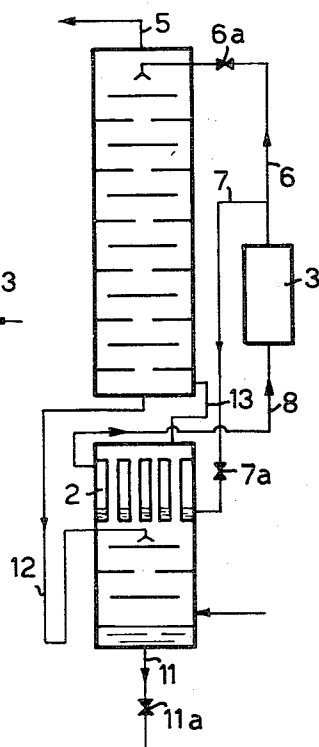


FIG.4



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2,820,769

PROCESS FOR PREPARING HYDROGEN-NITROGEN MIXTURES FROM COKE OVEN GAS

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Claims priority, application Great Britain April 7, 1955

10 Claims. (Cl. 252-374)

The present invention relates to the preparation of a mixture of hydrogen and nitrogen suitable for the synthesis of NH_3 using coke oven gas as the source of hydrogen.

A gaseous residue consisting essentially of hydrogen can be obtained from coke oven gas by cooling the gas under pressure, e. g. 10 to 30 atmospheres and -165° to -190° C., to condense therefrom less volatile components. The resulting gaseous residue contains, in addition to hydrogen, about 4% by volume of nitrogen, about 4% by volume of CO and, dependent upon the cooling, from 2 to 8% by volume of CH_4 . The present invention is particularly concerned with novel improvements for washing this impure gaseous residue with liquid nitrogen so as to remove CH_4 and CO substantially quantitatively.

It is customary for the washing of the gaseous residue to be carried out by flowing the residue through a washing column, while the residue is maintained under the pressure utilized in separating the less volatile components therefrom, in counter-current relationship to liquid washing nitrogen. In order to effect a high degree of CO removal, the temperature in the washing column must be very low although it may be varied within relatively wide limits depending upon the pressure utilized. As a specific illustration, a column temperature of about -190° C., can be utilized when the separating pressure is 13 atmospheres.

In order that the low temperature necessary for effecting a substantially complete removal of the CO may be maintained, it is customary to install a condenser, either in front, or on top, of the washing column, through which the gaseous residue is passed and cooled by the evaporation therein of liquid nitrogen under a constant pressure. Thus, if the separation of the coke oven gas is carried out at the usual pressure of about 13 atmospheres, the nitrogen in the condenser is evaporated at a pressure slightly higher than 1 atmosphere, namely, 1.3 atmospheres. As a result, the nitrogen in the condenser has a temperature of -193° C., and the gas mixture flowing through the condenser is cooled to a temperature which is slightly higher, namely, -190° C.

Both positions of the condenser, i. e. in front or on top, of the column, involve certain advantages and drawbacks. Thus, if the condenser is placed in front of the washing column, the gaseous residue from the coke oven gas separation enters the washing column at a temperature of about -190° C. Nearly immediately thereafter the temperature drops a few degrees owing to rapid evaporation of part of the washing nitrogen which goes into the gas mixture and takes up the volume of the methane, the latter being completely condensed at this low temperature. As a result, the temperature in the washing column is always lower than -190° C., so that it is possible to remove the CO nearly quantitatively to, e. g. 5×10^{-4} percent by volume by washing with relatively small amounts of liquid nitrogen.

The removal of CO depends not only on the tempera-

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ture but also on the reflux ratio in the washing column, i. e. the ratio between the amount of liquid nitrogen L flowing down and the amount of gaseous nitrogen V flowing upwardly with the gaseous mixture or residue to be washed. The amount of gaseous nitrogen V in the gaseous mixture depends upon the temperature prevailing in the column. For instance, with the gaseous residue obtained from every 1000 cu. m. coke oven gas flowing upwards through the washing column, the amount of nitrogen rising in the gaseous state V is:

56 cu. m. at -195°
102 cu. m. at -190°
185 cu. m. at -185°
258 cu. m. at -182°

In order to obtain the most economical consumption of liquid washing nitrogen possible the washing process is preferably carried out in such a way that L is equal to V or even slightly smaller (e. g. 5-10 cu. m.) than V. Expressed differently, the process is carried out under such conditions that the amount of washing nitrogen introduced into the washing column evaporates completely in the column and is removed at the top thereof together with the hydrogen freed of methane and CO, while the amount of liquid nitrogen collected at the bottom of the column, which is mixed with a large amount of CO, is equal to or slightly smaller than the amount of nitrogen continuously introduced into the washing column as part of the gaseous residue from the coke oven gas separation (about 4% by volume N_2).

If the condenser is placed in front of the column, the temperature in the column is very low. As a result, V has a relatively low value and L may also be small. Due to the relatively small values for L and V, the degree to which the CO is removed is highly dependent on fluctuations in the amount L and, moreover, the CO percentage of the washed hydrogen immediately rises to an undesired level when the amount of L becomes too small. Consequently, the advantage of installing the condenser in front of the washing column is that a constant and very low temperature prevails in the column with the result that the removal of CO is very effective if the correct amount of washing nitrogen is supplied. On the other hand, there is the disadvantage that the washing treatment requires great attention from the operating personnel since a small decrease in L, i. e. a decrease in the amount of liquid washing nitrogen supplied at the top of the column, immediately allows CO to pass out of the column admixed with the hydrogen.

If the condenser is placed on top of the column, the temperature in the washing column depends to a large extent on the temperature at which the gaseous residue of the coke oven separation is fed in at the bottom and a temperature which is too high to effect an adequate removal of the CO must be corrected by supplying a greater amount of liquid washing nitrogen.

Where the condenser is placed on top of the column, the temperature in the washing column is about 10° C. higher than in the case where the condenser is in front of the column and, as a result, the amount of gaseous liquid V flowing upwards is much greater. In order to obtain the lowest possible loss of nitrogen to the "residual gas" (the fraction which is collected and discharged at the bottom of the column in the liquid state), the amount of liquid nitrogen L flowing down in the washing column, which in this case is equal to the sum of the liquid nitrogen supplied at the top of the washing column and the condensate formed in the condenser, is chosen to be equal to V, or preferably to be even slightly smaller than V. Consequently, the value of L is much greater than in the case where the condenser is arranged in front of the column.

Due to the higher values of L and V when the condenser is placed on top of the column, the value of the reflux ratio L/V is much less sensitive to a decrease in L when compared with what would be the case at the same absolute drop in L if the condenser were placed in front of the column. In fact, it has been observed in practice that a washing column with the condenser placed on top requires less attention from the operating staff, as regards the feed of liquid washing nitrogen, than a washing column with the condenser placed in front. As a result of this, a negative $L-V$ can be safely maintained in the washing process so that the process carried out with a condenser placed on top of the washing column is extremely economical insofar as loss of nitrogen to the fraction of residual gas is concerned. On the other hand, there is the disadvantage that, as a result of the higher temperature in the washing column, the removal of CO is less thorough than in a washing column with the condenser arranged in front. Additionally, the washing column is particularly sensitive to temperature since there is no way of correcting the incoming temperature for the gaseous residue from the coke oven gas separation, for example, by means of a condenser in which liquid nitrogen is evaporated under a constant pressure. Consequently, a rise in the temperature of the gaseous mixture to be washed immediately results in a strong rise in the CO content of the washed gas.

It has now been found that if the condenser, in which the cooling is effected by evaporation of nitrogen under a constant pressure, is placed not on top or in front of the column, as previously proposed, but within it, or in such a way that two washing compartments are formed, which are separated by the condenser, the drawbacks of the above-mentioned washing systems are avoided and a hydrogen-nitrogen mixture of a very low CO content as well as a very reliable apparatus which requires little supervision are obtained. The loss of nitrogen to the "residual gas" fraction is very small and the CO removal is insensitive to temperature fluctuations in the arriving gaseous residue of the coke oven separation which is to be washed.

As regards the removal of CO by means of liquid nitrogen, it has already been proposed (see Dutch patent specification No. 74,830; French patent specification No. 861,175; U. S. patent specification No. 2,293,601) to use a washing column consisting of two washing compartments separated by a condenser and to feed as coolant into this condenser, the hydrogen under pressure and saturated with nitrogen coming from the top of the washing column, liquid nitrogen having been added to this hydrogen, before it enters the condenser. This liquid nitrogen must then evaporate under partial pressure to cool the gas mixture flowing through the condenser and rising in the washing column. However, in actual practice, the difference in temperature between the coolant and the gas stream to be cooled proves to be practically nil, so that liquid nitrogen is not evaporated and no cooling effect is obtained.

In contradistinction to the foregoing, the process of the present invention employs boiling liquid nitrogen as coolant in the condenser, the nitrogen being kept under a constant pressure preferably slightly higher than atmospheric, e. g. 1.05 to 1.60 atmospheres. In this way, a constant and very low temperature is maintained in the condenser.

The present invention is more fully explained by the attached drawing wherein Figures 1 and 2 represent prior art constructions and Figures 3 and 4 illustrate variations of the process and apparatus of the invention.

According to Figure 1, the cold gaseous residue of the coke oven gas separation is conducted to condenser 2 by means of conduit 4. The residue is cooled indirectly in the condenser by the evaporation of nitrogen supplied by the apparatus 3 wherein nitrogen is compressed to about 200 atmospheres and strongly cooled. The high-pressure nitrogen flows from apparatus 3 through conduit 7 and into the condenser after expansion thereof in valve 7a. The evaporated nitrogen is returned through conduit 8 into apparatus 3.

The gaseous residue of the coke oven gas separation, which is further cooled in condenser 2, flows through conduit 10 and into the bottom part of washing column 1. Liquid nitrogen is supplied to the top of the washing column through conduit 6 and valve 6a. Part of this nitrogen evaporates in the column while the remainder thereof is mixed with condensed methane and CO, discharged through conduit 11 and valve 11a, and evaporated by heat exchange with incoming coke oven gas as is the condensate formed in condenser 2 which is discharged through conduit 9 and valve 9a.

The hydrogen-nitrogen mixture freed of CO is discharged from the washing column through conduit 5 and, after heat exchange with arriving coke oven gas and the further addition of nitrogen to form a mixture of H_2 and N_2 in the volume ratio 3:1, is introduced into the NH_3 synthesis process.

In Figures 2-4, the parts corresponding to those in Figure 1 are denoted by means of the same reference marks as used in the latter figure.

In the apparatus of Figure 2, the condenser is placed on top of the column, so that the condensate formed in the condenser flows into the top part of the washing column. The cold residue of the coke oven gas separation flows directly through conduit 4 into the bottom section of washing column 1, in which it is washed by means of liquid nitrogen supplied through conduit 6. The washed gas flows through condenser 2, in which indirect cooling takes place by nitrogen evaporating in the condenser.

Figure 3 exemplifies the process and apparatus of the present invention. As shown therein, the cold gaseous residue of the coke oven gas separation first flows into the bottom section of a washing compartment 1a and subsequently through condenser 2 into washing compartment 1b. Liquid nitrogen supplied through conduit 6 is fed into the top section of washing compartment 1b.

The washing column may also comprise two separate parts, as is shown in Figure 4, which communicate by means of a U-shaped conduit 12, through which the washing liquid flows from one washing compartment into the other and by means of a conduit 13, which conducts gas. This latter embodiment offers the advantage that damping of the liquid in the condenser by arriving gas is impossible.

In the process of the invention, the combined height of the two washing compartments is not greater than the height of the washing column commonly used in the conventional construction with only one washing compartment. Furthermore, it has been found that the first washing compartment, located under the condenser, may be smaller than the second washing compartment. Thus, if the number of "theoretical plates" in the first washing compartment is about $\frac{1}{6}$ to $\frac{1}{4}$ of the total number of "theoretical plates" needed, the CO removal reaches its optimum value, under otherwise equal conditions.

The following table illustrates various CO contents for the washed gas, obtained when using apparatus according to Figures 1, 2 and 3 or 4 at different values of $L-V$.

The CO content relates to the eventual NH_3 -synthesis mixture (3 parts by volume of H_2 and 1 part by volume of N_2) obtained by making up the shortage of nitrogen after the washing treatment. The data given is based on passing at a pressure of 13 atm. the gaseous residue of 1000 cu. m. N. P. T. of coke oven gas, i. e. 620 cu. m. H_2 , 39.7 cu. m. N_2 , 41.8 cu. m. CO and 59.5 cu. m. CH_4 per hour through the apparatus. In all three cases, the temperature of the boiling nitrogen in the condenser was $-193^\circ C.$, so that the cooled gas mixture leaving the condenser had a temperature of $-190^\circ C.$ Accordingly, the temperature in the bottom section of the washing column according to Figure 1 was $-195^\circ C.$, while the temperature of the gas prevailing throughout the column of Figure 2 and in the lower washing compartment of Figure 3 was $-182^\circ C.$ In the second or upper washing

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compartment of Figure 3, the temperature was -190°C .

The total number of "theoretical plates" was equal in all three cases and amounted to 22.

L—V m. ³ NPT per 1,000 m. ³ coke oven gas treated	CO content with appa- ratus ac- cording to Figure 1 in percent by volume	CO content with appa- ratus ac- cording to Figure 2 in percent by volume	CO content with appa- ratus ac- cording to Figures 3 and 4 in percent by volume
5.....	2×10^{-3}	3.1×10^{-4}	4.2×10^{-5}
0.....	1.9×10^{-3}	5.2×10^{-4}	1.3×10^{-4}
-5.....	2.5×10^{-4}	9.3×10^{-4}	4×10^{-4}
-10.....	5×10^{-3}	1.8×10^{-3}	1.4×10^{-4}

From the above CO contents, it can be seen that the system according to the invention is considerably superior to the washing systems employed hitherto, particularly for negative values of L—V (which represents a very economical consumption of washing nitrogen). Furthermore, it is apparent that, when the process according to the invention is used, the removal of CO is far less sensitive to a decrease in the amount of washing nitrogen, which results in a fall of L—V, than when conventional systems are used.

It will be appreciated from the foregoing that the process described herein represents a novel improvement in the preparation of hydrogen-nitrogen mixtures from coke oven gas wherein the gas is cooled under pressure to condense low volatile constituents and the resulting cold gaseous residue consisting primarily of hydrogen and small amounts of nitrogen, carbon monoxide and methane is subsequently washed under pressure with liquid nitrogen. Broadly stated, the improved process of the invention comprises initially washing the cold gaseous residue by passing same upwardly through a first washing zone wherein the residue is washed by counter-current contact with liquid nitrogen, then passing the thus treated gaseous residue upwardly through an intermediate condensing zone wherein the residue is indirectly cooled with boiling nitrogen under a constant pressure preferably slightly higher than atmospheric and a condensate of nitrogen is obtained from the residue, thereafter further washing the gaseous residue by passing same upwardly through a second washing zone in counter-current contact with liquid nitrogen, collecting liquid washing nitrogen contaminated with carbon monoxide from said second washing zone and utilizing the collected nitrogen and the condensate from the condensing zone as the liquid nitrogen for washing the gaseous residue in the first washing zone.

According to the present process, the nitrogen utilized for washing in the second washing zone is substantially pure nitrogen. Preferably, the temperature of the gas being washed in the first and second washing zones is about -182°C . and -190°C ., respectively, although other temperatures include -175 to -188°C . in the first zone and -185 to -195°C . in the second zone. The temperature of the gas is, therefore, reduced by about 3 to 10°C . in the condensing zone. The pressure of the gas during the treatment is preferably the same as that used in initially condensing low volatile constituents from the coke oven gas, e. g. 10 to 30 atmospheres with 13 atmospheres particularly advantageous.

As shown in Figures 3 and 4, the apparatus of the invention, broadly described, comprises an upper gas washing compartment, means for supplying liquid washing nitrogen downwardly through the compartment in counter-current relationship to gas flowing upwardly there-through, means for collecting liquid washing nitrogen from the upper washing compartment, a lower washing compartment, means for passing gas to be washed upwardly and successively through the first and second washing compartments, condensing means for indirectly cooling said gas between the first and second washing compartments, the cooling means comprising boiling

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nitrogen under a constant pressure preferably slightly above atmospheric, means for collecting condensate obtained from the gas in said condensing means and means for supplying liquid nitrogen collected from the upper compartment and the condensate from the condensing means to the lower compartment as the wash liquid in the last-mentioned compartment.

It will be appreciated that various modifications may be made in the invention described herein. Hence, the scope of the invention is defined in the appended claims wherein:

I claim:

1. In a process for preparing hydrogen-nitrogen mixtures from coke oven gas by cooling said gas under pressure to condense low volatile constituents and thereafter washing the resulting cold gaseous residue under pressure by counter-currently contacting the same with liquid nitrogen to remove methane and carbon monoxide therefrom, the improvement which comprises initially washing said cold gaseous residue by passing same upwardly through a first washing zone wherein said residue is washed by counter-current contact with liquid nitrogen, then passing the thus treated gaseous residue upwardly through an intermediate condensing zone wherein said residue is indirectly cooled with boiling nitrogen under a constant pressure preferably slightly higher than atmospheric and a condensate of nitrogen is obtained from said residue, thereafter further washing said gaseous residue by passing same upwardly through a second washing zone in counter-current contact with liquid nitrogen, the height of said first washing zone being substantially less than that of said second washing zone, collecting liquid washing nitrogen contaminated with carbon monoxide from said second washing zone and utilizing the collected nitrogen and the condensate from said condensing zone as the liquid nitrogen for washing said gaseous residue in said first washing zone.
2. The process of claim 1 wherein the liquid nitrogen utilized for washing in said second washing zone is substantially pure nitrogen.
3. The process of claim 1 wherein said first and second washing zones are superimposed and the height of said first washing zone comprises from $\frac{1}{4}$ to $\frac{1}{4}$ of the joint height of said first and second washing zones.
4. The process of claim 1 wherein the pressure of the boiling nitrogen in said condenser is between 1.05 and 1.60 atmospheres.
5. The process of claim 1 wherein said gaseous residue is maintained at a pressure of 10 to 30 atmospheres during said washing and intermediate cooling steps.
6. The process of claim 1 wherein the pressure of the boiling nitrogen in said condenser is 1.3 atmospheres and the pressure of said gaseous residue during said washing and intermediate cooling is maintained at 13 atmospheres.
7. The process of claim 1 wherein the temperature of said gaseous residue is between -175 and -188°C . in said first washing zone and said residue is cooled about 3 to 10°C . in said intermediate condensing zone.
8. The process of claim 1 wherein the gaseous residue passed into said first washing zone consists essentially of, by volume, about 4% nitrogen, about 4% carbon monoxide, from 2 to 8% methane and the remainder hydrogen.
9. In a process for preparing hydrogen-nitrogen mixtures from coke oven gas by cooling said gas to a temperature of about -180°C . under about 13 atmospheres pressure to condense low volatile constituents therefrom and obtain a cold gaseous residue consisting essentially of, by volume, about 4% nitrogen, about 4% carbon monoxide, from 2 to 8% methane and the remainder hydrogen, and thereafter washing said cold gaseous residue at said pressure of about 13 atmospheres by counter-currently contacting same with liquid nitrogen to remove carbon monoxide and methane, the improvement whereby carbon monoxide and methane are substantially quantita-

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tively removed which comprises first washing said cold gaseous residue under about 13 atmospheres pressure and at a temperature of about -182°C . by passing same upwardly through a first washing zone in which said residue is washed by counter-current contact with liquid nitrogen; then passing the thus treated gaseous residue upwardly through an intermediate condensing zone wherein said residue is indirectly cooled to -190°C . by boiling nitrogen at a pressure of about 1.3 atmospheres and a temperature of -193°C . whereby a condensate containing nitrogen is obtained from said residue, thereafter further washing said cooled gaseous residue at about -190°C . by passing same upwardly through a second washing zone in counter-current contact with liquid nitrogen, the height of said first washing zone being substantially less than that of said second washing zone, withdrawing a gaseous mixture consisting essentially of hydrogen and nitrogen from said second washing zone, collecting the liquid washing nitrogen from said second washing zone, utilizing this collected nitrogen and the condensate from said condensing zone as the liquid nitrogen for washing said gaseous residue in said first washing zone.

10. Apparatus for preparing gaseous hydrogen-nitrogen mixtures from coke oven gas comprising an upper gas washing compartment, means for supplying liquid

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washing nitrogen downwardly through said compartment in counter-current relationship to gas flowing upwardly therethrough, means for collecting liquid washing nitrogen from said upper washing compartment, a lower washing compartment, the height of said lower washing compartment being substantially less than that of said upper gas washing compartment, means for passing gas to be washed upwardly and successively through said first and second washing compartment, condensing means for indirectly cooling said gas between the first and second washing compartments with boiling nitrogen under a constant pressure, means for collecting condensate obtained from said gas in said condensing means and means for supplying liquid nitrogen collected from said upper compartment and the condensate from said condensing means to said lower compartment as the wash liquid in said lastmentioned compartment.

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