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CHEMICAL PROCESS

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This invention relates to the art of thermally decomposing or cracking hydrocarbons at elevated temperatures and more particularly to cracking in the presence of certain protective coatings which I have found to be very efficient for preventing the corrosion of alloys containing 50% or more of nickel as the principal constituent with relatively smaller amounts of chromium with or without iron as a third major constituent and alloy steels containing more than 20 to 22% chromium with the addition of such modifying metals as nickel, manganese, molybdenum, etc.

It is well known that alloy steels containing nickel and chromium in varying proportions as their major constituents are useful for the construction of cracking tubes and chambers to be used at elevated temperatures. For example, their use for the construction of cracking chambers has been described in U. S. Patent 1,646,348 granted on October 18, 1927, to George O. Curme and in U. S. Patent 1,703,949, granted on March 5, 1929, to Stanley M. Norwood. However, it has been found that there is a marked difference in the properties of the alloys depending on the amount of chromium present. For example, if the amount of chromium is less than 20 to 22% by weight then the steel alloy lacks resistance to scaling and oxidation particularly when exposed for long periods of time to the high temperatures used in cracking hydrocarbons for the production of olefines; whereas, with steel having chromium present in amounts greater than 20 to 22% there is a marked improvement in the resistance to scaling and oxidation over long periods of time. The latter referred to alloy steels will be termed herein and in the claims as "high chromium alloy steels". The designation of the alloy steels in terms of its chromium content, namely, above or below 20 to 22% by weight, appears to be the simplest method of differentiating between the desirable alloy steels and those less desirable.

It is further known that alloys containing fifty per cent or more of nickel as the principal constituent together with relatively smaller amounts of chromium, with or without iron as a third major component, are also valuable in the high temperature cracking of hydrocarbons. This is disclosed in U. S. Patent 1,983,415, granted on December 4, 1934, to Charles T. Strosacker and Harold S. Kendall. These nickel alloys as defined above are known as nichromes and will be so designated herein and in the claims. Such alloys are also extremely resistant to oxidation and when formed into seamless tubes or tubes made by fusion welding of rolled strip, are practically ideal from the point of view of the scaling of the outside surface exposed to the furnace gases. They are very valuable for the construction of cracking chambers to be used for the pyrolysis of oil vapor or gas mixtures at metal temperatures up to 1000° C.

I have observed during the high temperature cracking of oil vapors in tubes made of high chromium alloy steels or of the nichrome alloys that the tubes are severely corroded in less than forty-eight hours when I am cracking raw untreated gasoline range distillates such as are obtained from a vapor phase cracking of various Mid-Continent residuum stocks. As an illustration of the extent to which this corrosion represents a serious handicap to the successful operation of a high temperature cracking unit, I state that I have had tubes of nichrome rendered entirely useless in thirty-six hours because of the development of cracks, pits and pinholes extending through the total wall thickness of one-eighth inch.

I have also observed that the corrosion rate is sufficiently high to completely ruin a cracking chamber in several days when thermally decomposing materials, such as virgin gas oil at temperatures above 700° C.

This invention has as its object the establishment and maintenance of certain protective coatings on high chromium alloy steels and on nichrome alloys, which we have found to be satisfactory as a surface for the thermal decomposition of hydrocarbons and which at the same time are extremely efficient in preventing the severe corrosion of these otherwise very valuable materials. A further object is the maintaining of said protective coating on said alloy. Another object is the prevention of corrosion in high chromium alloy steels and in nichrome cracking tubes when cracking sulfur-containing hydrocarbons regardless of its source. Still another object is the cracking of sulfur-containing hydrocarbons at temperatures in excess of 600° C. in high chromium alloy steel cracking chambers or in nichrome cracking chambers for long periods of time. Further objects will appear hereinafter.

The object of this invention is accomplished by cracking in the presence of high chromium alloy steels and nichrome upon the surface of which a protective coating is established by a treatment with steam or oxygen bearing gases. The protective coating may be established by pretreating the alloy prior to the cracking operation or it may be established during the crack-

ing. These protective coatings which appear to form during this pretreatment are extremely resistant to the corrosive action of sulfur-bearing hydrocarbons when they are cracked at elevated temperatures. These protective coatings may also be maintained, as one of the objects of this invention, through the continued or intermittent use of steam admixed in small amounts with the oil vapors being cracked.

As illustrations of the manner in which I thermally decompose hydrocarbons according to this invention, I present the following examples of methods of producing these protective coatings. They are not to be considered as statements of limitations to the practice of the invention.

Example 1

A nichrome V (eighty per cent nickel, twenty per cent chromium) cracking coil consisting of a cracking section of 121 feet of one inch inside diameter tubing and a soaking section of sixty feet 1½ inch inside diameter tubing is treated with steam alone for eight to ten hours at a maximum tube wall temperature of 800 to 850° C. Vapors of a raw gasoline range distillate containing 0.07% sulfur are then cracked in said nichrome cracking coil with approximately 5% by weight of steam admixed with said vapors. The cracking is carried on for several hundred hours in the presence of the protective coating which has been established by the steam pretreatment and which is continuously being maintained by the use of steam admixed with the oil vapors. No appreciable decrease in the wall thickness of the tube is observed.

Example 2

Vapors of a raw gasoline range distillate containing 0.07% sulfur were cracked without any addition of steam at the rate of approximately 375 pounds per hour and at a temperature between 725° and 775° C. in a nichrone V (eighty per cent nickel, twenty per cent chromium) cracking coil. The cracking coil consisted of a cracking section of 121 feet of one inch inside diameter tubing and a soaking section of sixty feet of 1½ inch inside diameter tubing. After a period of less than 48 hours, it was observed that the tube wall of ⅛ inch in the soaking section had been reduced to an average thickness of less than $\frac{1}{32}$ of an inch.

Example 3

Cracking tubes made of a high chromium alloy steel containing 22.4 per cent Cr, 10.6 per cent Ni, 1.25 per cent Mn, 0.14 per cent carbon are pretreated with air for six hours at a maximum metal temperature of 800° C. Gas oil vapors are subsequently cracked with not more than five to ten per cent of steam at a vapor temperature in excess of 700° C. and it is found that the cracking in the presence of the protective coating has prevented the corrosion of this alloy, which we have previously observed to take place at an average rate over the entire surface of more than 0.50 inch penetration per month.

Example 4

Nichrome tubes are used for the cracking of gasoline range distillate at 775 to 825° C. but the protective coating or layer is established almost simultaneously with the start of the cracking by using at least ten to fifteen per cent of steam admixed with the gas oil vapors. This method of operation is also found to give a surface layer which adequately protects the base metal of the tube against corrosion for practicable operating periods.

An essential feature of this invention is the thermal decomposition of hydrocarbon in contact with the protective coating or passive surface layer which I produce, for example, by pretreating the metal at an elevated temperature with steam or by adding a small amount of steam to the vapors to be cracked. This superficial layer protects the chromium bearing alloys referred to above, from which the cracking tube or chamber is constructed, against the severe corrosion we have frequently observed.

As further evidence of the effect of the protective coating in preserving the alloy and preventing severe corrosion the following summary of several tests is given below. The experiments were carried out by cracking a pressed wax distillate containing sulfur at a temperature of 800° C. while in contact with nichrome V. The hydrocarbon in each instance was of the same composition.

Test No. 1

Cracking pressed wax distillate alone, no attempt being made to form a protective coating.

Time of test..... 17 hours.
Loss in weight due to corrosion.. 21.0% per day.

Test No. 2

Cracking pressed wax distillate in the presence of 5.4% steam.

Time of test..... 23.5 hours.
Loss of weight due to corrosion..... none.

Test No. 3

The nichrome V was pretreated for 6.0 hours at 850° C. with steam. The pressed wax distillate was then cracked without steam.

Time of test..... 18.5 hours.
Loss of weight due to corrosion.. 0.25% per day.

A comparison of Test No. 1 with Test No. 2 shows the effectiveness of a small amount of steam in preventing corrosion. Test No. 3 shows the ability of steam to build up a protective coating which is temporarily effective against corrosion.

The following tests were made in order to determine whether or not the corrosion was due to the presence of sulfur in the hydrocarbon being cracked. The experiments were carried out by cracking hydrocarbons having different sulfur content at a temperature of 800° C., and in contact with nichrome V in each instance and no attempt was made to form a protective coating on the alloy.

Test No. 4

A gasoline range distillate containing 0.069% by weight of sulfur was cracked at 800° C. while in contact with nichrome V.

Time of test..... 20.5 hours.
Loss in weight due to corrosion.. 30.7% per day.

Test No. 5

Aviation grade gasoline containing less than 0.005% by weight of sulfur was cracked at 800° C. while in contact with nichrome V.

Time of test..... 18.0 hours.
Loss in weight due to corrosion... 3.8% per day.

Thus the corrosion rate was markedly decreased by using a low sulfur gasoline.

Although the above examples represent the preferred embodiments of this invention, the invention is not limited by the scope of the various conditions or sequence of steps set forth in the examples. The protective coating may be formed by other means than that of treating the alloys with steam, although the use of steam is preferred and considered to be the most desirable and most effective method. For example, the alloy may be pretreated with air or carbon monoxide prior to cracking for sufficient length of time to form a substantial protective coating. In the case of air, temperatures in excess of 700° C. should be used while with carbon monoxide, temperatures of about 1000° C. should be used.

I have found, as illustrated in Example 4 above, that the alloy does not necessarily have to be pretreated in order to gain some protective action which will prevent corrosion. The data below presents evidence that even when using a small amount of steam with oil vapors to be cracked in tubes made of nichrome, for example, the original metal surface is immediately modified to such an extent, by the formation of some protective layer, that corrosion is markedly inhibited. This data was obtained by suitably exposing samples of the material having equal surface areas so that it is possible to express the results as per cent loss in weight per day.

Test No.	Parts of steam per 100 parts of oil	Loss in weight percent per day
6	0.0	30.7
7	2.3	6.7
8	4.8	4.3
9	23.0	Nil.
10	45.9	Nil.

It is thus possible by the methods embodied in this invention to merely effect the thermal decomposition with steam in varying amounts and build up a protective layer which will either partially or completely inhibit the corrosion of the basic metal of the cracking tube.

Steam, when admixed with the hydrocarbon being cracked, may be used in any amount sufficient to obtain the formation of the protective coating. When the formation of the steam is solely for the purpose of preventing corrosion it is desirable to have same present in amounts ranging between 5 and 15% by weight of the hydrocarbon to be cracked. The steam may be admitted to the system at any point prior to the cracking step.

This process is adapted for the cracking of hydrocarbons at high temperatures. By the term high temperatures as used herein and in the claims are those temperatures that result in the production of a high yield of gaseous olefines. In this sense I am not concerned with temperatures below 600° C. Preferably the cracking step is carried out at a temperature above 650° C.

The methods embodying this invention are applicable for the thermal decomposition of sulfur bearing hydrocarbon materials regardless of its source. For example, the material may be a vapor derived from a gas oil, a pressed wax distillate or a low boiling gasoline range distillate or the material may be an essentially pure saturated or unsaturated gaseous hydrocarbon or mixtures thereof.

It may not be desirable to crack the hydrocarbon in the presence of steam and in such cases it is within the spirit of this invention to merely treat the metal intermittently with steam or by any other means which will establish the protective coating. In addition to the above tests I present the following to illustrate that such a procedure will give a real protection against corrosion. I treated a specimen of nichrome with steam for six hours at 850° C. and obtained a protective coating which was resistant to the action of the corrosive agents in pressed wax distillate when this material was cracked for 18.5 hours at 800° C. without steam. The specimen lost only 0.19 per cent by weight, whereas when it had not been pretreated it lost almost twenty per cent by weight over the same period of exposure.

In the process of pretreating the alloy comprising the cracking chamber with steam prior to cracking so as to establish thereon a protective coating it is recommended that the treatment be carried out at an elevated temperature, and for a sufficient length of time to create thereon said coating. In order to expedite the formation of the coating it is recommended that temperatures in excess of 600° C. be used. I have found that it is preferable to use a temperature of about 850° C. for this pretreating step. After the chamber has been used for some time the protective coating becomes ineffective and it is necessary to stop the cracking process and pretreat with steam so as to recreate said protective coating, thus the process may be carried out by the intermittent process of cracking and steam treatment. As a variation, however if it is possible to use steam during the cracking operation it might be desirable to first, pretreat with steam in order to create a protective coating, and then maintain that protective coating by the addition of small amounts of steam to the cracking gases. In this variation, I find it preferable to add steam at an amount of about 5% by weight of the mixed vapors.

The uses to which the methods embodied in this invention may be put are more or less obvious. If I wish to thermally decompose hydrocarbon vapors, which are corrosive at elevated temperatures, for the production of olefins, I can best do so by cracking in the presence of protective coatings established and maintained by the methods of this invention. This invention clearly discloses the manner in which these valuable chromium bearing alloys may be successfully used for such high temperature cracking operations.

The advantages are also very easily discernible. I have found that it is impossible to use a nichrome alloy tube, for example, for the thermal decomposition of a material such as gasoline range distillate without completely destroying the tube by corrosion. I have also demonstrated that high chromium alloy steels are similarly attacked by the same and other cracking stocks. The methods embodied in this invention therefore represent an improvement in the art of high temperature cracking since they make it possible to use these alloys which are particularly valuable, as pointed out above, from the point of view of creep and resistance to scaling.

By the phrase highly heat-resistant chromium alloy, as used herein and in the claims, the applicant means those alloys of the class consisting of nichromes and high chromium alloy steels.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. In the process of producing olefins by thermally decomposing a sulfur-bearing hydrocarbon at a temperature above 600° C. while in contact with a highly heat-resistant chromium alloy, the improvement which comprises contacting said alloy prior to the cracking process with steam at a temperature sufficiently high and for a sufficient length of time to create thereon a protective coating.

2. A process in accordance with claim 1 characterized in that the treating of the alloy with steam is carried out at an excess of 700° C. and below 1000° C.

3. In the process of producing olefins by thermally decomposing a sulfur-bearing hydrocarbon at a temperature above 600° C., while in contact with nichromes the improvement which comprises contacting said nichromes prior to the cracking process with steam at a temperature sufficiently high and for a sufficient length of time to create thereon a protective coating.

4. In the process of producing olefins by thermally decomposing a sulfur-bearing hydrocarbon at a temperature above 600° C., while in contact with high chromium alloy steel the improvement which comprises contacting said high chromium alloy steel prior to the cracking process with steam at a temperature sufficiently high and for a sufficient length of time to create thereon a protective coating.

5. In the process of producing olefins by thermally decomposing sulfur-bearing hydrocarbon at a temperature above 600° C., while in contact with a highly heat-resistant chromium alloy, the improvement which comprises contacting said alloy prior to the cracking process with steam at temperature sufficiently high and for a sufficient length of time to create thereon a protective coating, proceeding with a cracking operation and then stopping the cracking operation when the protective coating becomes ineffective and retreating with steam so as to recreate said protective coating, thus repeating the intermittent process of cracking and steam treatment.

6. In the process of producing olefins, by thermally decomposing a sulfur-bearing hydrocarbon at a temperature above 600° C., while in contact with a highly heat-resistant chromium alloy, the improvement which comprises contacting said alloy, prior to the cracking process, with steam at a temperature sufficiently high and for sufficient length of time to create thereon a protective coating, then proceeding with the cracking operation, adding to the cracking gases a small amount of steam so as to maintain said protective coating.

7. In the process of producing olefins, by thermally decomposing a sulfur-bearing hydrocarbon at a temperature above 600° C., while in contact with nichrome, the improvement which comprises contacting said nichrome, prior to the cracking process, with steam at a temperature sufficiently high and for sufficient length of time to create thereon a protective coating, then proceeding with the cracking operation and, adding to the cracking gases a small amount of steam so as to maintain said protective coating.

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