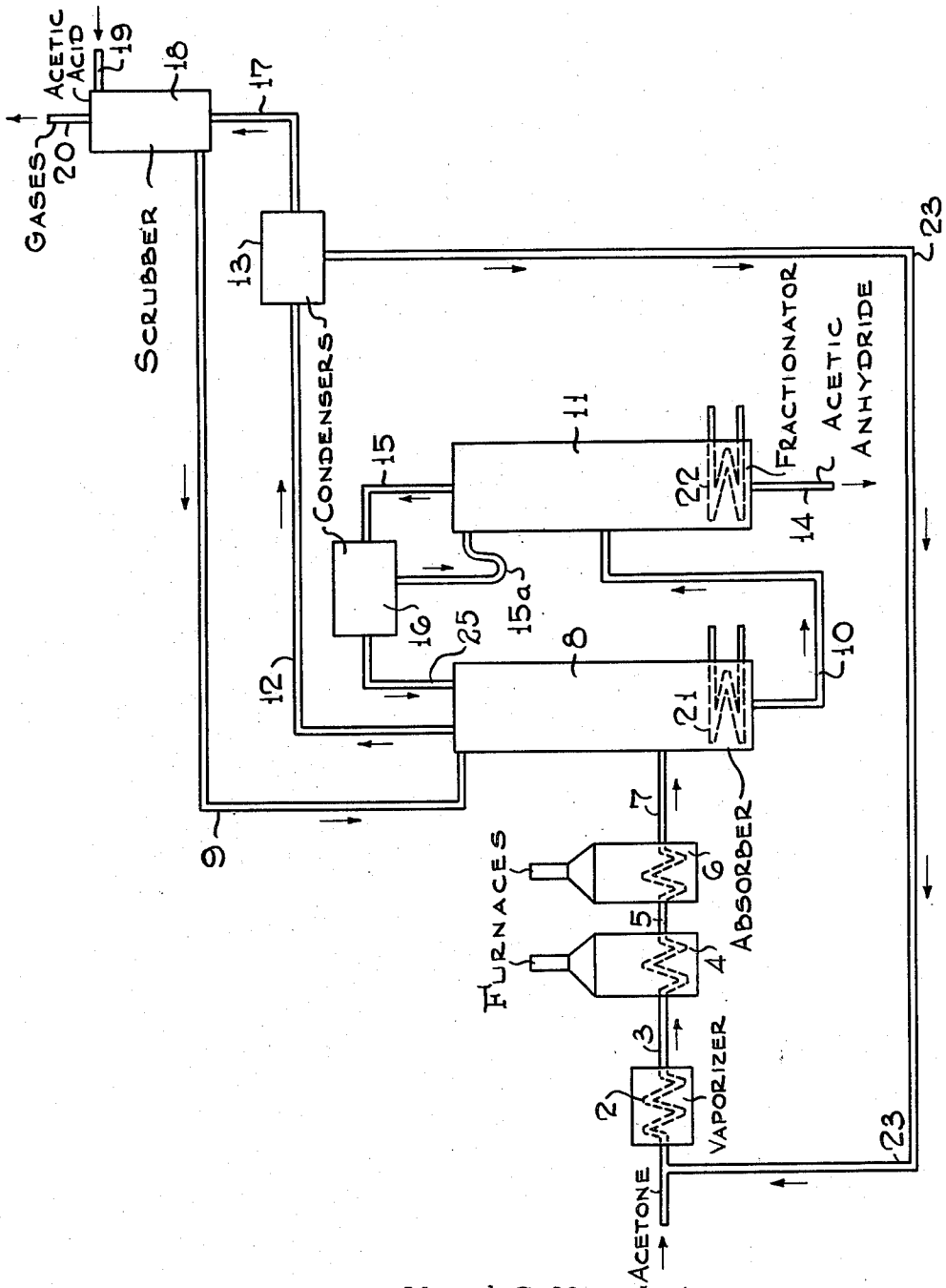
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PREVENTION OF COKE FORMATION
IN PYROLYSIS OF ACETONE
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PREVENTION OF COKE FORMATION IN PYROLYSIS OF ACETONE

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This invention is directed to a process for treating apparatus for carrying out reactions, such as are used in the production of gases and vapors by the distillation and cracking of materials containing them, in the vapor or liquid phase in metal wall reaction chambers or in the presence of metal parts or elements. More particularly, this invention relates to the conditioning of alloy steels containing high percentages of chromium and nickel which are to be used in the distillation and cracking of materials in the vapor or liquid phase.

In commercial processes in which organic compounds are distilled or cracked in tubes, vats, chambers or containers composed of ferrous alloys containing high percentages of chromium and nickel, it is a well-known fact that the high nickel content of the reaction chamber surfaces results in the formation of excessive amounts of coke which soon fills the tubes, vats, chambers or the like, necessitating costly shutdowns for purposes of cleaning out the coke.

It is, therefore, the main object of this invention of provide a method for conditioning the surfaces of a high chrome-high nickel steel prior to its use in the cracking of organic compounds so as to substantially reduce or even to eliminate coke formation.

According to the present invention the above difficulties due to coking are overcome by subjecting the inside surfaces of the metal tubes to a novel conditioning treatment which involves a starting-up procedure using controlled conditions of repeated cracking and regeneration. The invention contemplates the practice of reaction processes of the character referred to, by preliminarily giving this treatment to the metal surface or to the interior surface of the metal piping, vat, chamber or container which is to be employed in the reaction process so as to condition the metal surface and thereby prevent excessive coking when the metal surface is subsequently used in the above-described process.

The invention will be described in connection with the process of cracking ketenizable material such as acetone, acetic acid, acetic anhydride or the like, to produce ketene, but this is intended to illustrate the method and the invention is not intended to be limited to such use. In general, all the prior art processes either definitely state, or by setting forth examples indicate that the pyrolysis of acetone or other ketenizable material should be carried out in carbon, copper, quartz, or silver pyrolysis apparatus. While copper is satisfactory because of its non-catalytic activity with

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respect to ketene, from the structural standpoint and for high temperature use, copper presents certain disadvantages. For example, it may become necessary to sheathe or otherwise protect the copper reaction chamber in order to prolong its life. Furthermore, copper oxidizes during periods of regeneration and is not structurally strong. A high-chrome-no-nickel steel fails upon repeated heating and cooling, unless tempered by slowly heating or cooling each time. This is impractical in an emergency shutdown, for example, when the temperatures have to be dropped rapidly. Carbon steel is unsatisfactory because it causes severe coking and is not capable of withstanding temperatures over 1100° F. A high-chrome-low-nickel steel such as an 18-8 chrome-nickel alloy is unsuitable for the same reason although it can take a slightly higher temperature. Consequently it has been found desirable to use a high-chrome-high-nickel steel in the reaction chambers when pyrolyzing a ketenizable material to ketene. For example, an alloy of the following composition has been found to be particularly suitable:

23-27% chromium
12-20% nickel
Less than 0.2% carbon
Balance substantially iron

Such a material has the advantage over copper in that it is not oxidized at operating temperature and it has the advantage over silver in costs. Yields may be obtained that are as good as any obtained by using copper or silver.

For better appreciation of the invention, reference is made to the accompanying drawing in which numeral 2 represents a vaporizer means for acetone, which may be a simple coil as shown, or a metal stillpot or the like. The vaporizer is connected by line 3 to preheater 4 which likewise may be of simple construction, comprising merely a S-coil or the like.

The preheater 4 is illustrated as a coil of large diameter to provide low pressure drop and may be composed of the alloy described above. However, it may, if desired, consist of rows of straight tubes connected in series or parallel by means of return bends or headers. It is connected by conduit 5 to pyrolysis chamber 6 which may be a single tube or coil or other type of enclosed chamber, but is of less diameter than the preheater and is composed of the alloy described above. Chamber 6 is connected by line 7 to absorption tower 8 which may be of any convenient construction.

Tower 8 is provided with conduit means 9 for introducing acetic acid to be reacted with the ketene and with draw-off means 10 at the base of the column connected with fractionator 11. The upper part of the absorber is provided with vapor take-off means 12 connecting with condenser 13. Fractionator 11 is provided with bottom draw-off means 14 and vapor take-off conduit 15 which passes through condenser 16 to the top of absorber 8. Part of the condensate from condenser 16 is returned to fractionator 11 through line 15A for reflux and at least a part is preferably passed to absorber 8 through line 25. Condenser 13 is connected with line 17 to scrubber 18 which is provided at its top with means 19 for introducing scrubbing liquid and vent line 20 for removing gase and connects at its bottom with line 9 into the absorber 8. The liquid condensed by condenser 13 is recycled by line 23 back to the feed inlet to the vaporizer and preheater zones. Means are provided in absorber 8 and fractionator 11 for supplying heat, such as steam coils 21 and 22.

In operating the process of this invention for the continuous cracking of acetone, a positive gage pressure of about five pounds is maintained on the apparatus but with an inlet temperature of the gas to the cracking zone of about 1150° to 1200° F. and an outlet temperature for the vapors of about 1300° F.–1400° F. when acetone is being cracked. The contact time of vapors with cracking temperatures should preferably be between 0.25 and 0.75 second, and the vapors preferably should have a mass velocity in the cracking zone of about 10-40 lbs./sq. ft./sec.

If the above appartus is immediately used for the cracking of acetone under the above conditions, the tubes of pyrolysis chamber 6 soon become plugged with coke. If, however, the tubes of chamber 6 are first submitted to closely controlled conditions of acetone cracking and treatment with steam and air, the tubes become conditioned and no longer plug up with coke. In order to accomplish this conditioning acetone is introduced into coil 6 at 10–50 lbs./sq. ft./sec. mass velocity, with a contact time of 0.1 to 1.0 sec. and temperatures between 1150° and 1400° F. It is essential that the flow rate and pressures be held constant during the cracking operation and under some conditions it is desirable that the temperature be increased slowly from 1100° F. up to the final temperature used. The rate of rise should be about 10 to 50° F. per hour.

As soon as coking sets in, as indicated by increased pressure across the reaction tube, the acetone feed is cut off, the coil is flushed with an inert gas and subjected to treatment with a mixture of steam and air at temperatures between 1600° and 1800° F. until the coke is removed (regeneration). The treatment with acetone and then with steam and air is repeated under the same conditions after cooling, at least once and preferably several times with a maximum total of about six after which the temperature in the regeneration step is reduced to 1400°–1500° F. and the same sequence of steps, under these reduced temperature conditions, are repeated until cracking occurs without pressure increase across the cracking coil. The above sequence of steps can be carried out with the temperature in the regeneration step maintained throughout between 1400 and 1500° F. The conditioning may be hastened by using a fast temperature start-up during the cracking step, that is, the temperature is taken from below the cracking range of about 1100° F. to the final cracking temperature in from fifteen minutes to one hour.

In actual pilot plant operation, a new coil of the above composition was conditioned by the following operations:

1. Regeneration with steam and air at 1550° F.

2. Cracking of acetone at 1200–1300° F. followed by regeneration at 1750° F. with steam and air. This was repeated three times more, with cooling to 1100° F. prior to each cracking step.

3. Cracking of acetone at 1200–1300° F. followed by regeneration at 1450° F. with steam and air. This was repeated once.

After the above steps, cracking of acetone was started with no deposition of carbon in the tube and with very low dehydrogenation indicated.

While it is not intended to limit this invention by any theory as to what occurs by the above described treatment, metallurgical examination of the conditioned tubes indicated that a thin skin around the inner surface of the tube had been changed by the addition of extraneous carbon not present in the original metal and that carbon originally present in the metal had been precipitated on the grain boundaries. X-ray diffraction patterns did not show conclusively what the nature of the thin inner protective surface was, but it is believed that carbide formation had occurred.

A tube conditioned in the above manner should not be cleaned by mechanical means since it has been found that if the conditioned surface is scratched it is necessary to start the conditioning process again in order to prevent coking. It is, therefore, preferable to burn out any deposits in the tube rather than scrape or bore them out.

The above-described conditioning process while described in detail as applied to the cracking of acetone to produce ketene, is equally applicable to other pyrolytic processes, such as the dehydrogenation of butane, in which high-chrome-high-nickel steels are required for structural strength at the high temperatures necessary for the reaction, but in which the nickel or chromium may catalyze undesirable side reactions.

The nature and objects of the present invention having thus been fully described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. In a process for the manufacture of ketene by the pyrolysis of acetone wherein a chemical reaction in a ferrous metal container, the inside surface of which is composed of 23–27% chromium, 12–20% nickel, and the balance substantially iron, results in excessive coke formation of the inner surface of the container, the method of conditioning said surfaces and preventing said excessive coke formation which comprises preliminarily contacting said surface with acetone at a temperature between 1150° and 1400° F. until excessive amounts of coke are formed on the surface, subjecting the coke-covered surface of a regeneration treatment with steam and air at a temperature between 1600 and 1700° F. until the coke is removed, repeating the pyrolyzing and regenerating steps several times under the same conditions and then repeating the same steps for several more times while maintaining a temperature of 1400–1500° F. in the regeneration step until coke no longer forms on the surface.

2. In a process for the manufacture of ketene by the pyrolysis of acetone wherein a chemical reaction in a ferrous metal container, the inside surface of which is composed of 23–27% chromium, 12–20% nickel, and the balance substan-

tially iron, results in excessive coke formation of the inner surface of the container, the method of conditioning said surfaces and preventing said excessive coke formation which comprises preliminarily contacting said surface with acetone, while increasing the temperature from 1100° F. up to a temperature not lower than 1150° F. and not over 1400° F. at the rate of 10° to 50° F. per hour, maintaining the final temperature reached while continuing to treat with acetone until excessive amounts of coke are formed on the surface, subjecting the coke-covered surface to a regeneration treatment with steam and air at a temperature between 1600° and 1700° F. until the coke is removed, cooling the coke-free surface to 1100° F., repeating the pyrolyzing and regeneration steps several times under the same conditions and then repeating the same steps for several more times while maintaining a temperature of 1400° to 1500° F. in the regeneration step until coke no longer forms on the surface.

3. In a process for the manufacture of ketene by the pyrolysis of acetone wherein a chemical reaction in a ferrous metal container, the inside surface of which is composed of 23–27% chromium, 12–20% nickel, and the balance substantially iron, results in excessive coke formation of the inner surface of the container, the method of conditioning said surfaces and preventing said excessive coke formation which comprises preliminarily contacting said surface with acetone while rapidly increasing the temperature from 1100° F. up to a temperature not lower than 1150° F. and not over 1400° F. within 15 minutes to one hour, maintaining the final temperature reached, while continuing to treat with acetone, until excessive amounts of coke are formed on the surface, subjecting the coke-covered surface to a regeneration

treatment with steam and air at a temperature between 1600° and 1700° F. until the coke is removed, cooling the coke-free surface to 1100° F., repeating the pyrolyzing and regeneration steps several times under the same conditions and then repeating the same steps for several more times while maintaining a temperature of 1400–1500° F. in the regeneration step until coke no longer forms on the surface.

4. Process according to claim 1 in which each and every regeneration step is carried out at 1400–1500° F. throughout the conditioning treatment.

5. Process according to claim 2 in which each and every regeneration step is carried out at 1400–1500° F. throughout the conditioning treatment.

6. Process according to claim 3 in which each and every regeneration step is carried out at 1400–1500° F. throughout the conditioning treatment.

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