

July 5, 1966

E. S. PAINTER ETAL

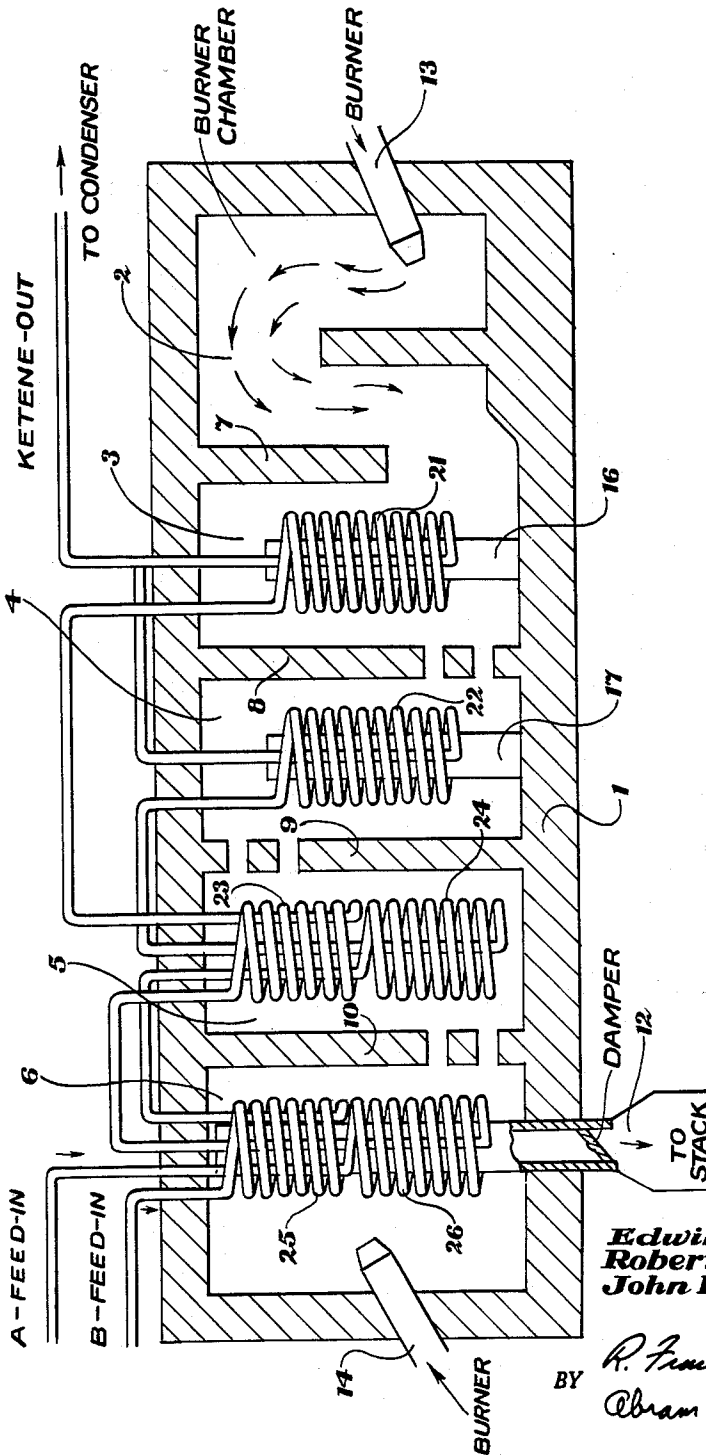
3,259,469

APPARATUS FOR MANUFACTURING KETENES

Filed July 26, 1961

2 Sheets-Sheet 1

Fig. 1



Edwin S. Painter
Robert C. Petrey
John H. Jensen, Jr.
INVENTORS

BY R. Frank Smith
Abram W. Hatcher
ATTORNEYS

July 5, 1966

E. S. PAINTER ETAL

3,259,469

APPARATUS FOR MANUFACTURING KETENES

Filed July 26, 1961

2 Sheets-Sheet 2

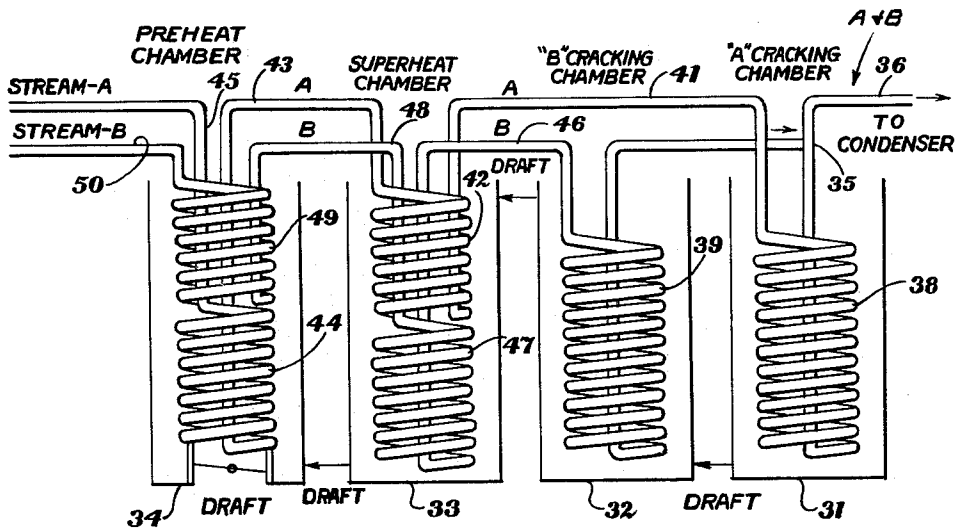
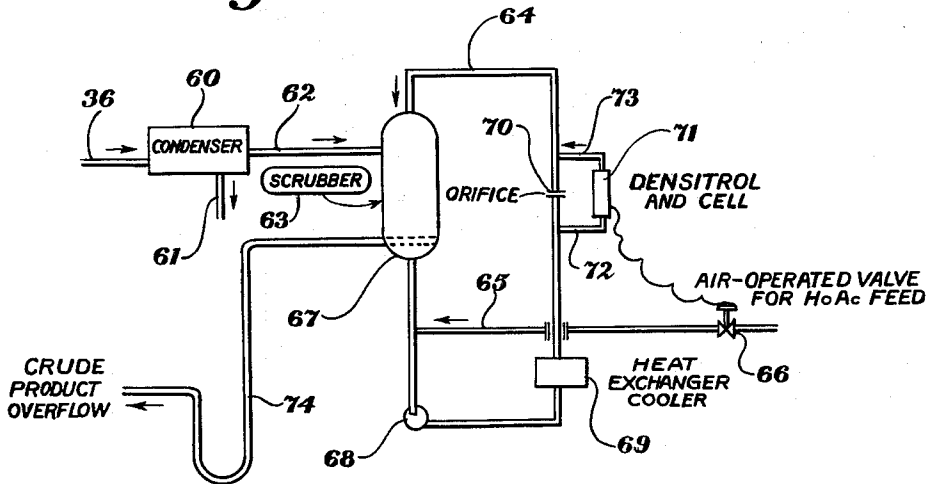


Fig. 2

Fig. 3



Edwin S. Painter
Robert C. Petrey
John H. Jensen, Jr.
INVENTORS

BY *R. Frank Smith*
Abraham W. Hatcher
ATTORNEYS

1

2

3,259,469

APPARATUS FOR MANUFACTURING KETENES
Edwin S. Painter, Robert C. Petrey, and John H. Jensen,
Jr., all of Kingsport, Tenn., assignors to Eastman Kodak
Company, Rochester, N.Y., a corporation of New
Jersey

Filed July 26, 1961, Ser. No. 126,937
2 Claims. (Cl. 23-277)

This application is a continuation-in-part of application
Serial No. 31,441, filed May 24, 1960, now U.S. Patent
No. 3,136,811.

This invention relates to the manufacturer of ketenes
and anhydrides. More particularly, this invention con-
cerns apparatus for the manufacture of ketene by the py-
rolysis of acetic acid and the conversion of the ketene to
acetic anhydride.

The manufacture of ketenes and anhydrides by the py-
rolysis of various compounds such as acids, ketones and
other ketenizable materials is practiced on a large scale in
the industry. A number of patents and publications de-
scribe processes and apparatus pertaining to such subject
matter.

For example, our co-workers' Patents 2,258,985 and
2,393,778 describe one and two chamber furnaces and
processes for the pyrolysis of various ketenizable organic
compounds. A three chamber furnace is described in U.S.
Patent 2,541,471. In Painter Patent 2,784,065 (one of the
inventors herein) another embodiment of a three chamber
furnace is disclosed. Such prior processes and apparatus
are quite efficient and produce satisfactory pyrolysis prod-
ucts. However, it is apparent from the economic stand-
point that the development of apparatus whereby the yields
of ketene and the like products from pyrolysis may be in-
creased and more uniform products obtained represents a
highly desirable result.

After extended investigation we have found an appar-
atus arrangement whereby the yield of ketene may be in-
creased, costs of operation reduced and other advantages
obtained as will be described in detail hereinafter.

This invention has for one object to provide a more
efficient apparatus for the manufacture of ketenes. A
particular object is to provide an improved apparatus for
the pyrolysis of acetic acid to ketene. Another object is
to provide a better device for use in converting ketene to
acetic anhydride whereby more uniform results may be
secured. A special object is to provide a new arrange-
ment whereby the over-all yield of ketene may be in-
creased. Still another object is to provide a novel appar-
atus arrangement which permits more efficient results and
provides a reduction in costs of operation and expense of
more expensive materials. Another object is to provide an
apparatus of the class indicated wherein there is provided a
special cracking coil arrangement. Other objects will ap-
pear hereinafter.

As pointed out above and as may be noted by reference
to the patents referred to or other publications, the crack-
ing of ketenizable materials has frequently been accom-
plished in two chamber or three chamber furnaces. Ex-
pressed in another way, there has been employed in cer-
tain instances two coils and a crucible or three coils. In
general it is known from past experience that some in-
crease in efficiency may be accomplished by increasing the
size of the furnace from a two chamber to a three cham-
ber construction. This is usually attained to some extent
because of better heat utilization and for similar reasons.
Accordingly, it was expected that some improvement
should be secured by advancing from a three coil process
and apparatus to a four coil or chamber setup. However,
such four chamber unit, when constructed and piped in a
manner generally comparable to the best performing three

chamber furnaces, did not give an efficiency of operation
to the degree which seemed desirable. While such four
chamber units piped in accordance with prior construc-
tions were entirely operative and produced good products
in substantial yields, the increase in production was only of
the order of that attributable to the added chamber.

After extended investigation we found that if a four coil
or chamber furnace was modified in certain respects, not
only in certain details of construction, but in particular
with respect to the piping, that a much higher degree of
efficiency could be obtained. Such increase was substan-
tially greater than could be attributed to the addition of
the further chamber. In particular we have found that
the cracking coil arrangement in a four chamber furnace
could be considerably different from the arrangement hereto-
fore used in prior constructions.

In the broader aspects of our invention we have found
that, in a four chamber furnace, if two cracking coils are
in parallel, one in the third chamber and another in the
fourth chamber, quite unusual results may be secured.
These parallel cracking coils are connected in series with
the preheating and superheating coils in chambers 1 and 2
of said four chamber furnace. By this new arrangement
of coils and associated parts, we have found that an in-
crease of production of ketene may be secured to the
order of 40% greater than the production of ketene from
a four chamber furnace and operated like a three chamber
furnace of the prior art.

A further understanding of our invention may be had
from a consideration of the attached drawing forming a
part of the present application.

FIG. 1 is a semidiagrammatic side elevation view in sec-
tion illustrating a four chamber furnace embodying the
coil arrangement of the present invention. As will be ap-
parent hereinafter, since many of the details of construc-
tion may be the same as presently used construction for
such type of furnaces, extended description of FIG. 1 will
not be necessary.

FIG. 2 is a more fully diagrammatic side elevation view
in a particularly simplified form for illustrating the piping
and coil arrangement in a four chamber furnace of the
present invention. This figure has been presented in
particular to illustrate the basic inventive features of the
instant invention.

FIG. 3 is a semidiagrammatic side elevation view of an
anhydride forming unit such as may be used in conjunc-
tion with the furnaces of the present invention. That is,
the ketene produced in the furnaces of the present inven-
tion may be utilized in the process and apparatus of FIG.
3 for the production of a uniform anhydride product.

Referring now to FIG. 1, it can be noted that many
of the parts shown in this figure may be the same or
similar to the parts described in companion Patents
2,541,471 and 2,784,065 and that the materials of con-
struction may be the same as described in these patents.
The furnace is comprised of a furnace housing 1 which
would be of suitable ceramic or brick work for enclosing
the several coils for preventing heat escape and also for
bringing the heating medium in close contact with the
coils. The interior of this furnace housing is divided into
four chambers 3, 4, 5 and 6. Each of these chambers
are separated from the other chambers by suitable baffle
wall 7, 8, 9 and 10. These ceramic baffle walls may be
of any desired construction such as the various construc-
tions disclosed in 2,541,471 and 2,784,065 just referred
to. Chamber 6 is provided with an exit 12 whereby the
heating gases may be exhausted to a stack (not shown).

In the construction shown in FIG. 1, the combustion
chamber is provided with one or more burners 13. How-
ever, supplemental to or in lieu of the combustion chamber,
individual burners may be inserted into each of the

3

chambers 3, 4, 5, etc. In such arrangement the burners are preferably positioned to discharge tangentially to the walls and not to impinge directly on the coils in the chamber. Similar remarks apply to burner 14 in that it would be angled so as not to impinge directly on the coils 25 and 26.

In addition to the refractory baffles and the like just referred to, in at least chambers 3 and 4, and if desired, in the other chambers, there would be provided refractory core members such as 16 and 17 which core members are encircled by the cracking coils to be described in detail hereinafter. Extended description of these core members which may be solid or tubular, is unnecessary inasmuch as the construction thereof may be substantially exactly in accordance with the disclosure in companion Patent 2,541,471.

In each of these chambers of the four chamber furnace there are positioned coils and piping through which is fed the katenizable material to be cracked or pyrolyzed to ketene. That is, cracking coils 21 and 22 are positioned in chambers 3 and 4. Superheating and preheating coils 23, 24, 25 and 26 are positioned in the other two chambers 5 and 6. A further understanding of this coil arrangement and positioning, which is an important part of the present invention, will be had from a consideration of FIG. 2 which will now be described.

In this schematic and simplified view of FIG. 2, it will be observed that there has been provided the areas 31, 32, 33 and 34 corresponding to the four chambers referred to above. Such areas or chambers have been further identified by the legends appearing on FIG. 2 as cracking chamber, superheating chamber and preheating chamber.

In connection with the cracking chamber it will be noted that in addition there have been designated the capital letters A and B corresponding to stream A and stream B noted on the left of FIG. 2. In the arrangement of the present invention the piping and coil construction is such that two streams, namely A and B of the katenizable material may be fed through the four chamber furnace simultaneously, the two streams joining at point 35 at the single conduit 36 after leaving the furnace.

An important feature of the piping and coil arrangement of the present invention is that chambers 31 and 32 each contain a cracking coil 38 and 39 piped in parallel.

Considering cracking coil 38, this is connected by conduit 41 to the superheat coil 42, which superheat coil is connected by conduit 43 to the preheat coil 44. This preheat coil leads back through conduit 45 to the feed (stream A) of the katenizable material.

In a similar manner, cracking coil 39 is connected by a conduit 46 to a superheating coil 47. It will be noted that this superheating coil 47 is positioned below coil 42 of line A. However, the particular coil that is above or below the other coil is not an undue limitation on the present invention. In general, it is preferred that if the coil of line A is at the top of the superheat chamber, then the coil of the same line would be at the bottom of the preheat chamber inasmuch as such arrangement provides for better heat distribution.

Continuing further with the piping of stream B, it will be observed that the superheat coil 47 is connected by conduit 48 to the preheat coil 49 which coil leads into the feed of stream B through conduit 50.

From this simplified piping diagram it will be observed that two streams A and B of katenizable material may be fed into the four chamber furnace of the present invention. In each instance each stream A and B is subjected to approximately comparable preheating and superheating treatment in the chambers 34 and 33. Then each of the streams A and B enters its separate cracking chamber 32 and 31 wherein the final pyrolysis takes place. The resultant pyrolysis products are united at point 35 to the single conduit 36 through which the pyrolysis products are conducted to a condenser and other treatments to separate and/or utilize the products.

4

We have discovered that the capacity of the furnaces of the class under description is limited both by pressure drop in the tubing and by heat input to the furnace. We have found that the new arrangement of the present invention providing two cracking coils in parallel and otherwise in accordance with the arrangement of FIG. 2 has reduced the pressure drop for a given flow rate and allowed an increase in feed of 40%. Expressed in another way, by the new piping arrangement of the present invention the pressure drop obtained is equivalent to the pressure drop obtained in a conventional three coil furnace.

Referring now to FIG. 3, we have disclosed process and apparatus by which the ketene produced by the present invention may be utilized. The ketene leaving the furnace through conduit 36 may be passed into a condenser 60, the condensables are withdrawn at 61. The ketene gas thus preliminarily treated passes through conduit 62 into scrubber 63. In this scrubber the ketene gas is contacted with a circulating stream of a mixture of acetic anhydride and acetic acid entering the scrubber through conduit 64.

Acetic acid is admitted to this scrubber system through the supply line 65 which supply line contains therein automatic valve 66. The reaction product of the ketene with the acetic acid withdrawn from the bottom of the scrubber at point 67 is pumped by pump 68 through heat exchanger 69 and then through the orifice device 70. This device is associated with the control system 71 which is interconnected with valve 66 aforementioned. The reaction product overflows from scrubber 63 through conduit 74.

The control device functions to automatically measure the specific gravity of the flowing stream which is bypassed at a suitable temperature, e.g. about 30° C., through lines 72 and 73. Such measurements are based on the specific gravity and the operation of valve 66 in response thereto permits the automatic control of the reaction product of the ketene with the acetic acid to an accuracy within $\pm 0.3\%$ expressed in terms of the concentration of acetic acid in the mixture of acetic acid and acetic anhydride. This permits the utilization of the ketene for making a more uniform acetic anhydride.

A still further understanding of our invention will be had from a consideration of the following examples which are set forth to illustrate certain of our preferred embodiments of operation.

Example I

In accordance with this example a comparison is made between operation in accordance with the present invention and operation by the older (prior art) procedure.

	Old Procedure (1)	New Procedure (2)
Pressure drop.....	-----	Same as in old.
Temperature.....	-----	Do.
Cu. ft. in coils.....	23.3	25.3
Outside surface.....	397 sq. ft.	398 sq. ft.
Production as acetic anhydride.....	65,000 lbs./day	91,000 lbs./day.
Contact time.....	-----	0.66 of the old.
Time in cracking chamber.....	.078 sec.	.112 sec.
Fuel gas usage.....	2.25 cu. ft./lb. Ac ₂ O.	2.5 cu. ft./lb. Ac ₂ O.

According to operation in accordance with the new procedure of the present invention, each of the first two coils is divided into two separate halves and each of the two parallel flow paths passes through $\frac{1}{2}$ in each furnace chamber as shown in FIG. 2. Preferably in order to equalize the heat transfers in the two paths, one path traverses the half-coil in the hotter end of one chamber (i.e., the end at which the hot gases enter) and through the half-coil in the cooler end of the next chamber. As indicated above, there is little preference as to which chamber is reversed in this regard with respect to the other.

To supply additional heat for the increased capacity obtained by the present invention, auxiliary gas-fired burners are used in the first chamber, now known as the preheat

chamber. The use of burners in such chamber increases the temperature of the flue gas leaving the furnace. As already indicated above, when burners are inserted in the chambers, they are preferably positioned so the flame will not impinge directly on the coils. The fuel gas usage as indicated was 2.25 cu. ft. per lb. of anhydride on procedure (1) and is 2.5 cu. ft. per lb. of anhydride on procedure (2). In addition to the 40% increase in production, an 11% increase in gas usage per pound of anhydride produced was incurred.

In further detail as may be noted by reference to FIG. 2 stream A and stream B flow in parallel through the preheat chamber, superheat chamber and then stream A goes to the fourth chamber designated the "A" cracking chamber and stream B goes to the third chamber designated "B" cracking chamber. Stream A goes to the bottom half of the preheat chamber and the top half of the superheat chamber while stream B goes to the top of the preheat chamber and to the bottom of the superheat chamber.

The hot combustion gases from the "A" cracking chamber leave this chamber at the bottom and enter the "B" cracking chamber at the bottom and leave at the top thereof. The waste gases leave the superheat chamber at the bottom and enter the preheat chamber. The preheat chamber coils have a shell inside the coil. The hot gases entering at the bottom of the preheat chamber travel upward around the coils and outside the shell and enter the shell at the top of the chamber and travel down past the draft damper on to a steam generator and the waste gas stack (not shown).

In the present example, gas burners are fired in the annular space around the coil in the preheat chamber supplying additional heat. As indicated in the above table, in the pyrolysis of acetic acid as streams A and B and the conversion thereof to acetic anhydride the present invention gave about a 40% increase in rate of production of anhydride.

Example II

In accordance with this example an apparatus in accordance with FIG. 1 and having the coil arrangement of FIG. 2 was employed for carrying out the conversion of acetic acid to ketene. Feeds "A" and "B" were comprised of glacial acetic acid of approximately 99.95% purity. The acetic acid, as it entered the preheat chamber of FIG. 2, had injected therein a small amount of catalyst. That is, there was incorporated in the acetic acid feed a small amount of phosphate catalyst. Suitable catalysts are trimethyl phosphate, tri-isopropyl phosphate and tripropyl phosphate and other phosphate esters of this type. Streams A and B which are in series in the preheat and superheat chambers were subject to a temperature in the preheat chamber within the range of 700-800° C. In the superheat chamber the temperature range was within the range of 900-1100° C.

In the cracking chambers where the coils are in parallel arrangement, the temperature was within the range of 900-1100° C. The heat was supplied by several burners positioned in all the chambers as needed to supply sufficient heat by burning natural gas to maintain the temperatures specified aforesaid in the respective chambers.

The pressure drop with the piping and coil arrangement of the present invention, from the point of entry before the feed of the preheat zone to the exit at conduit 36 was of the order of 240 mm. As may be noted, such pressure drop is relatively low and compares favorably with the pressure drop of two and three chamber furnaces.

The rate of feed of the glacial acetic acid to the process in each separate line in accordance with this example was of the order of 2700 lbs. per hour. The conversion of such feed to ketene was of the order of 80-85%.

The ketene produced in accordance with this example was reacted with acetic acid in an apparatus as diagrammatically disclosed in FIG. 3 to give a high quality uniform acetic anhydride. As described above in connection

with FIG. 3, the reaction of the ketene and acetic acid is controlled by continuously withdrawing a sample stream of the reaction product and measuring the specific gravity by means of a controller obtained commercially under the name of Densitrol. Such controller is sold by the Precision Thermometer and Instrument Company of Philadelphia, Pennsylvania. By such controlled reaction wherein the feed of the acetic acid reacted with the ketene is controlled by the specific gravity of the reaction product, there was obtained a very uniform acetic anhydride.

Expressed in another way, operating in accordance with the present example wherein the pyrolysis was accomplished in a four chamber furnace with the two cracking coils in parallel, there was obtained 91,000 lbs. per day of relatively uniform acetic anhydride. This represents approximately a 26,000 lb. per day increase of production over a four chamber furnace which was piped and otherwise operated in accordance with prior art procedures.

The following further examples are set forth to illustrate different feed rates, different temperature ranges of the preheat, superheat and cracking zones and the like variations in our process. However, apparatus as described above in detail was used.

Example III

With the temperature of the acid stream leaving the cracking chamber at 740° C. and a feed rate of 2700 pounds of acid per hour, a production rate of 88,000 pounds per day of acetic anhydride was obtained.

Example IV

With the temperature of the acid stream leaving the cracking chamber at 730° C. and a feed rate of 2700 pounds of acid per hour, a production rate of 86,000 pounds per day of acetic anhydride was produced.

Example V

With an acid stream temperature leaving the cracking coil at 740° C. and a feed rate of 2900 pounds of acetic acid per hour, a production rate of 89,000 pounds of acetic anhydride was produced per day.

Example VI

With the temperature of the acid stream leaving the cracking chamber at 730° C. and a feed rate of 2900 pounds per hour, a production rate of 88,000 pounds of acetic anhydride per day was obtained.

Example VII

In operating the furnace as per the conditions shown in Example II but using acetone as a feed, a conversion of 90% is obtained with a production of 90,000 pounds of acetic anhydride while feeding 62,000 pounds of acetone.

In the above examples the furnace construction, interior partition walls and the like were of refractory material such as high temperature fire bricks. The piping and coils were constructed of chromium steel containing refractory encircled by the coils as described in the above-mentioned Patent 2,541,471. In general we prefer to construct the coils and piping of a chromium-aluminum steel or chromium-nitrogen steel as shown in U.S. Patent 2,393,778. However, certain stainless steel as Type 446 may be used. Also Types 405, 406, 430 and 440 may be used in some instances when necessary.

Although the process has been described primarily with respect to the conversion of acetic acid to ketene, this being one of the principal types of conversions carried out commercially, our apparatus may be utilized in the pyrolysis of other ketenizable materials exemplified by acetone, ethyl acetate, propionic acid and other ketones, acids and esters of this type.

It is thought apparent from the foregoing that we have provided a new and improved piping and coil arrange-

ment which is specially adapted for four chamber furnaces for the production of ketene from the pyrolysis of acetic acid whereby increased production capacity may be obtained from the apparatus without increased floor space or the use of larger quantities of the heat resistant chromium containing steel used to prepare coils. Also, we have shown that the ketene produced may be readily converted to a relatively uniform acetic anhydride.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An apparatus useful for the production of ketene by the pyrolysis of a ketenizable organic compound, said apparatus comprising a furnace housing which encloses at least four communicating chambers, gas heating means for heating said furnace, an exit channel for exhausting gas from said gas heating means from the interior of the housing to an exhaust stack, baffle walls within the housing for dividing the interior of the housing into said at least four chambers, said chambers comprising a preheating chamber, followed by a superheating chamber, followed by two cracking chambers, the apparatus being further characterized in that said preheating chamber contains two coils, one in the bottom portion and the other in the top portion of said preheating chamber, said coils being extensions of two feed conduits without the housing, said superheating chamber containing two coils, one in the bottom portion and the other in the top portion of said superheating chamber, said coils being connected to the first-mentioned two coils of said preheating chamber by two separate conduits, one of which leads from the lower end of the coil in the top portion of the preheating chamber to the upper end of the coil in the bottom portion of the superheating chamber and the other of which leads from the lower end of the coil in the bottom portion of the preheating chamber to the upper end of the coil in the top portion of the superheating cham-

ber, thereby providing substantially uniform heat distribution throughout both preheating and superheating chambers, a cracking coil in each of said two cracking chambers, one of said cracking coils being connected to one of said coils in the superheating chamber, and the other cracking coil being connected to the other coil in the superheating chamber, conduit means from each of the two cracking coils leading to a single exit conduit outside the housing through which exit conduit the ketene product from the apparatus may be conducted to further processing means.

2. The furnace of claim 1 wherein the further processing means comprise a scrubber for receiving the ketene product, said scrubber being joined by a conduit to and in juxtaposition with a density-regulated automatic control device whereby the specific gravity of the ketene product passed through the scrubber is automatically measured, said conduit leaving the bottom and entering the top of said scrubber, said density-regulated automatic control device comprising an air-operated valve actuated by a density-measuring unit positioned along a line which by-passes an orifice in said conduit, and a feed conduit for introducing acetic acid to the scrubber system.

References Cited by the Examiner

UNITED STATES PATENTS

2,196,767	4/1940	Hasche	23—277
2,541,471	2/1951	Hull et al.	23—277
2,688,635	9/1954	Eberts et al.	260—585 X
2,695,836	11/1954	Gilmore	23—3
2,776,192	1/1957	Painter et al.	23—277
2,784,065	3/1957	Painter	23—277
2,890,930	6/1959	Steele et al.	23—2

MORRIS O. WOLK, *Primary Examiner.*

MAURICE A. BRINDISI, *Examiner.*

A. J. STEWART, J. SCOVRONEK,
Assistant Examiners.