(12) **EUROPEAN PATENT SPECIFICATION**

(54) MAKING NON-PUFFING PETROLEUM COKE BY DELAYED COKING.

Making non-puffing petroleum coke by delayed coking

BACKGROUND OF THE INVENTION

Electrode grade graphite is manufactured from a commercial grade of coke having an acicular, anisotropic microstructure called needle coke, see U.S.—A—2,775,549, made by delayed coking of certain petroleum residues under specific conditions of heat and pressure. To produce graphite from
5 such coke, it is necessary to heat it to a temperature in the range of 2000—3000°C, which has the dual function of supplying energy for the conversion of the carbon in the coke to the graphitic crystalline form and of volatilizing impurities. When carbon bodies made from such cokes are heated at temperatures in the vicinity of 1000—2000°C, various sulfur-containing compounds decompose, attended by a rapid and irreversible expansion of the carbon body. This phenomenon is termed "puffing". During the
10 production of graphite articles, particularly high performance graphite electrodes, puffing is extremely undesirable as it may destroy the structural integrity of the piece and render it marginal or useless for its intended purpose.

Puffing of a carbon article made from high sulfur cokes generally starts at about 1500°C, and may result in a volumetric expansion of as much as 25%. It is not simply an elastic expansion but
15 should be characterized as an inelastic, irreversible expansion.

The generally accepted explanation of the puffing phenomenon is that in acicular needle cokes with a relatively large amount of sulfur, sulfur atoms are bonded to carbon atoms by covalent bonds, either in carbon ring structures or linking rings. These bonds are less stable at high temperatures than the carbon-to-carbon bonds. On heating, the carbon-sulfur bonds rupture, the sulfur is freed, then
20 reacts with hydrogen to form hydrogen sulfide. The simultaneous rupture of these bonds and evolution of hydrogen sulfide and other sulfur containing materials causes the physical expansion called puffing.

Puffing has been avoided in the past by using coke made from petroleum residues low in sulfur content. This approach is of only limited utility at present since the principal petroleum crudes currently in use have high sulfur contents, and the cokes made from their residues will normally exhibit an
25 undesirable degree of puffing.

Another approach to elimination or alleviation of the puffing problem in manufacture of graphite articles has been by the use of additives. These additives have usually been added during the mixing stage when various sizes and grades of coke particles are mixed, before being wetted with pitch, formed into the desired shape, baked at an intermediate temperature and graphitized at high tempera-
30 tures. Additives have included primarily metal salts and oxides, as disclosed in GB—A—733,073, FR—A—1,491,497, FR—A—2,035,273, U.S.—A—3,642,962, U.S.—A—3,563,705, U.S.—A—3,842,165, and U.S.—A—3,338,993.

The patents above disclose the use of iron, sodium, chromium, nickel, cobalt, boron aluminum, titanium, calcium, zirconium, manganese, magnesium, barium and strontium compounds as puffing
35 inhibitors. Some compounds of this group are in general usage and of these a choice is naturally made based upon the effectiveness as a puffing inhibitor and upon other properties of the graphite article such as electrical resistivity, tensile strength, modulus of rupture, modulus of elasticity, coefficient of thermal expansion, and cost.

Of the above, FR—A—1,491,497 discloses the use of chromium oxide at 0.2—5% in a mixture
40 with coke and a binder as a catalyst, enabling graphitization to occur at temperatures in the range of 1200°—2000°C.

FR—A—2,035,273 discloses a low sulfur coke produced by the addition of 0.3—5% of sodium carbonate to the coking stream mixture and subsequent hydrogenation of the coke at high temperature.

GB—A—733,073 discloses the use of oxides of chromium, iron, copper or nickel incorporated in
45 the grinding stage of coke, mixed with pitch, shaped, baked at 1200°C, and graphitized at 2500°—2800°C.

U.S.—A—3,563,705 discloses the use of mixtures of iron or calcium compounds with small amounts of titanium or zirconium compounds as puffing inhibitors incorporated into the coke-binder mixture.
50 U.S.—A—3,338,993 discloses the use of calcium, magnesium, strontium, and barium fluorides as puffing inhibitors with raw of calcined coke and binder, mixed, shaped, baked and graphitized.

U.S.—A—3,642,962 discloses the use of 1—3% calcium cyanamid or calcium carbide as desulfurizing agents and puffing inhibitors, mixed wirh raw coke prior to calcining.

US—A—3 873 427 teaches the combination of a ferruginous material and a metal chloride as a
55 desulfurizer for coal and coke but is silent on the production of a non-puffing coke.

At present, the most common methods of the above are those using iron oxides mixed dry in the coke-pitch binder blend as puffing inhibitors. These are effective puffing inhibitors but must be used with caution, as their use tends to increase the coefficient of thermal expansion or CTE, of the finished product, to an undesirable level.
60 CTE is also of vital importance in the production of graphite for certain applications. Electrodes for electric furnace melting of steel must have a low CTE to avoid excessive differential expansion at operating temperatures and the resultant spalling,which in turn causes excessive consumption of the

electrode and cost in operation. Other applications requiring dimensional stability at high temperatures are well-known although of somewhat less economic importance.

In general, the addition of any foreign material to a graphitizing carbonaceous mix will have, in addition to its desired effect, such as puffing inhibition, the effect of increasing the CTE of the graphite body.

A needle coke is distinguished by its physical structure when microscopically examined, showing long needle-like acicular particles. Such cokes, to be suitable for manufacture of graphite electrodes to be used in ultra-high powered electric steel furnaces, should have a graphite CTE characteristic of less than $5 \times 10^{-7}/°C$ measured over the range of $0°—50°C$. Needle cokes for lower powered electric steel furnaces may have a graphite CTE characteristic of as much as $7 \times 10^{-7}/°C$ over the $0°—50°C$ range.

The blends of cokes must be thoroughly mixed to avoid the difficulties present in making uniform homogeneous blends and in thoroughly coating the particles, which are often as much as 7 mm. in diameter, with the puffing inhibitor. Both of these difficulties can lead to non-uniform dispersion of the inhibitor and to puffing, even though there is sufficient inhibitor present in the total mix to prevent puffing.

This non-uniformity is particularly troublesome when operating under the newer type of graphitization processes, which raise the temperature of the carbon bodies (i.e. electrodes) at a much higher rate than the older processes. The combination of high sulfur with high rate of temperature rise exacerbates the problem and requires more stringent treatment to overcome puffing.

It should be emphasized that overcoming the puffing problem becomes increasingly more difficult in the larger graphite electrode sizes (above 51 cm (20 in.) diam) because in such sizes, larger particles of coke are used. Since the puffing inhibitor only coats the surface of the particles, the coke surface area to inhibitor weight ratio decreases (for a given weight addition ratio), giving a higher concentration of inhibitor on the coke particle surfaces for the larger particle blends. Thus a large amount of the inhibitor is at relatively greater distance from the centers of the coke particles in the larger coke particle mixes as opposed to the smaller particle mixes used in smaller electrodes. Migration of the inhibitor into the centers of the large particles becomes progressively more difficult and less effective as the coke particles increase in size.

The puffing problem is further increased with the rate of graphitization of the carbon bodies. Optimum distribution of the inhibitor throughout the structure of the carbon body to be graphitized is essential as the degree of puffing for any coke particle blend is highly rate sensitive, being directly related to the rate of temperature increase during the graphitization cycle. Thus, the figures in certain of the examples given will show a much higher dynamic puffing at a 14°C/min. temperature rise than for a 5°C/min. rise.

The amount of puffing for any given coke-inhibitor blend could be expressed as a proportionality in the general form:

$$DP = \frac{k(S, P, \Delta T)}{1}$$

where DP = dynamic puffing
  S = sulfur content of coke
  P = mean particle size
  ΔT = rate of temperature increase
  1 = amount of inhibitor
  k = proportionality factor

Thus it may be seen that increases in sulfur content, particle size, and temperature rise will increase puffing, while an increase in the inhibitor level will decrease puffing.

SUMMARY OF THE INVENTION

A petroleum coker feedstock which would normally produce a puffing coke due to its high sulfur content is rendered non-puffing by the addition of a small quantity of puffing inhibitor to the feedstock as a fine particle size powder.

Puffing inhibitors such as iron oxide and/or calcium fluoride may be pre-dispersed in a high concentration in a small quantity of the feedstock (fresh feed or furnace feed), or in compatible material miscible with the feedstock, or dispersed in the total coker stream and added either batchwise to a batch type coker, or continuously to the main stream in a delayed coker.

The use of a fine particle size powder of 100% less than 5 micron diameter, pre-dispersed in a portion of the feedstock, insures that the final product will be a homogeneous coke with puffing inhibitor uniformly distributed throughout.

A current of inert gas or steam bubbled through the batch type coker during the run aids in keeping the puffing inhibitor in suspension without significantly increasing the CTE of the finished product during batchwise coking. In a commercial delayed coker this is not essential. For a description

3

of delayed coking, reference is made to an article by R. J. Diwoky, *Continuous Coking of Residuum by the Delayed Coking Process*, Refiner and Natural Gasoline Manufacturer, Vol. 17, No. 11, Nov. 1938. The present invention involves the use of this type of coking operation.

5 Iron oxide is formed when any of numerous iron bearing materials is calcined, including organo-metallic compounds and salts. Minerals such as magnetite (Fe_3O_4), limonite ($2Fe_2O_3 \cdot 3H_2O$); and pyrites (FeS_2) and salts such as ferric sulfate and nitrate when roasted in air are converted to ferric oxide, and may be used to form the oxide.

The reactive species may be elemental iron, produced by reduction of the Fe_2O_3 by coke during graphitization.

10 Calcium fluoride is also highly effective as an inhibitor with slightly superior performance as compared to iron oxide. Mixtures of the two inhibitors have shown a synergistic result, being more effective than either of the two when used alone.

The addition of inhibitor in this manner to the feedstock to the coker produces a coke which is lower puffing and produces a graphite which has a lower CTE than from a coke conventionally inhibited 15 by a dry mix.

The mode of operation of these puffing inhibitors is probably a scavenging reaction, sulfur reacting with the metallic ions to form the sulfides, then decomposing slowly at higher temperatures to give a controlled evolution of vaporized elemental sulfur.

In general the use of any of the additives listed above, when added to a coke particle-pitch binder 20 mix, will lower the extent of puffing, but at the same time significantly increase the CTE, of the graphite bodies made from such cokes. I have found that the use of puffing inhibitor dispersed in the coker feedstock in appropriate amounts prior to coking gives an unexpected advantage in that it controls puffing of the coke while increasing the CTE only to a smaller degree (or in some instances not at all), when compared to the CTE of a graphite body in which the puffing has been eliminated by adding the 25 same additive to the electrode mix by the conventional dry-mix practice.

CTE of the graphitized coke was determined by preparing small 1.6 × 12.7 cm (5/8″ × 5″) electrodes by the procedure disclosed in U.S.—A—2,775,549 (except for calcination of the coke to 1250°C), and measuring their elongation over the temperature range of 0° to 50°C.

30 DESCRIPTION OF THE PREFERRED EMBODIMENT

In figure 1 a decant oil, the fractionater tower bottoms from a catalytically cracked gas oil fraction, also termed slurry oil, or other equivalent hydrocarbon residue, is conveyed from the fractionater 33 through line 10 and meter 14 to diversion valve 17, where a portion of the feedstock is diverted through valve 13, and meter 15 to disperser 18. Simultaneously a portion of inhibitor 12 is weighed in 35 scale 16 and conveyed to disperser 18 where it is dispersed in the feedstock to a specific concentration by weight. Alternately a compatible liquid and additives from supply 19 are metered through valve 11 to valve 13 and meter 15 to disperser 18. The inhibitor is dispersed and discharged through line 22 and meter 23 to mixer 24 where it is mixed with the main portion of the feedstock coming through line 20 and meter 25, to the exact proportion desired. The concentrate mixed with the feedstock is pumped by 40 pump 27 through line 26 to furnace 29, then through line 31 to coker drums 28 and 28A, where it is conventionally delay coked. The overheads are taken off through line 32 and sent to the fractionater 33.

In the above flowsheet, 18 is the disperser which may be any of several types of equipment well known in the art, preferably a high shear or colloid mill. Alternately, a roller or ball mill could be used.

In practice, a dispersion of approximately 5—50% by wt. of puffing inhibitor in the feedstock is 45 used as a concentrate.

The puffing inhibitor dispersion and feedstock are metered into the mixer 24 where they are mixed in the correct proportions to give a concentration of approximately 0.05—0.5 wt. % puffing inhibitor in the feedstock which is then pumped into the coker 28.

At the operating temperatures the viscosity of the feedstock is extremely low and some means is 50 necessary to minimize settling and a concentration of the puffing inhibitor in the lower portion of the coker during batchwise coker operation. I have found that by the introduction of a small flow of inert gas bubbled up from the bottom of the coker drum, I can maintain the puffing inhibitor in a uniform suspension without significantly raising the CTE of the finished product or lowering the acicular crystal content of the coke. This is not necessary if the invention is carried out in a commercial delayed coker.

55 The following are examples of specific methods of practicing the invention:

Example 1

The micronized puffing inhibitors, calcium fluoride and iron oxide (having approximately the same particle size distribution) were individually mixed with samples of a fresh feed decant oil coker 60 feedstock, at 0.1 wt. % level in a high speed blender for about 5 minutes. The mixtures were coked under identical conditions in 4 liter resin flasks.

In an insulated glass resin flask, an inert gas at the rate of 4.5 l/h/kg (0.16 SCFH/kg) mixture was bubbled up from the bottom of the coking pot to keep the inhibitor uniformly dispersed in feedstock.

65

The following time-temperature cycle was used:

Temperature	Elapsed Time	Rate ΔC°/hr
Room to 350°C	3 hours	110
350—450°C	4.5—5 hours	20
450°C	16 hours	—
450—530°C	4.0—4.5 hours	20
530°C	1 hour	—
530°C to ambient temperature	Cool-down, power off	

Dynamic puffing of the cokes was then determined in comparison with uninhibited samples, and with samples inhibited in the normal manner with dry-mixed iron oxide. The coke samples had 50% < 0.074 mm. particles and 100% < 0.088 mm. particles.

Puffing was measured by taking representative samples by the method of ASTM D346—35, crushing, mixing 100 g coke and 25 g pitch, and molding plugs at 86197.5 k.Pa. (12,500 psi). The plugs were measured by micrometer and placed in a dilatometer. The temperature was raised to 1200°C over a period of 50 ± 10 min., then the test was run at a temperature increase of 5° or 12—16°C/min. over the 1200°—2900°C range, with measurements taken every five minutes. The reported DP is the maximum degree of elongation (or shrinkage) measured. All of the DP's below were at 14°C/min. rise except as noted.

Inhibitor Added to Feedstock	Coke Yld. %	Ash %	S %	CTE × 10^{-7}/°C** % Fe_2O_3*		DP, % Δ L*** % Fe_2O_3*	
				0	$\frac{1}{2}$	0	$\frac{1}{2}$
0	23.3	0.01	1.17	3.0	—	+6.8	—
0	23.3	0.01	1.17	—	3.8	—	+1.7
0.1% CaF_2	24.9	0.65	1.26	4.2	—	+1.2	—
0.1% Fe_2O_3	23.0	0.50	1.22	4.1	—	+1.6	—

* (Iron oxide dry-mixed into the coke)
** (Coefficient of Thermal Expansion over the range of 0°—50°C × 10^{-7}/°C, 5/8″ × 5″ (1.6 × 12.7 cm.) sample, 10 min. time)
*** (Dynamic Puffing over the range of 1200°—2900°C)

Of the two puffing inhibitors, the calcium fluoride was found to be the more effective. The addition of either inhibitor to the feedstock significantly decreased puffing of the resulting coke. The CTE of the resulting cokes was within the range (under 5 × 10^{-7}/°C considered necessary for a needle coke.

For less demanding applications, a CTE of the graphite body of as much as 7 × 10^{-7}/°C may be acceptable, but for ultra high power electrodes for electric steel furnaces the upper limit is generally 5 × 10^{-7}/°C.

Example 2

Another fresh feed sample was tested as in Example 1 using the inhibitors at a higher level of addition, with the following results:

Inhibitor Added to Feedstock	Coke Properties	
	CTE $10^{-7}/°C$	DP, $\% \, \Delta \, L$
0	2.9	8.3
CaF_2 (0.2%)	4.7	0.7
Fe_2O_3 (0.2%)	5.1	0.7

Some feedstocks may well need and be beneficially treated with inhibitor additions of as much as 0.5%, resulting in a 2% ash level in the final coke.

The examples above are not shown as limitations but merely samples from the wide variety of petroleum residues currently available.

Claims

1. A process for the manufacture of a non-puffing needle coke having a graphite CTE characteristic of not higher than $7 \times 10^{-7}/°C$. over the range of 0° to 50°C. suitable for conversion to electrode grade graphite by delayed coking of petroleum feedstocks having a level of sulfur content combined molecularly in components of said feedstock sufficiently high enough to contribute to an irreversible volumetric expansion on heating to a temperature of 1400°C or higher, in the presence of a puffing inhibitor, characterized by the dispersion of from 0.05 to 0.5% by weight of a puffing inhibitor which is iron oxide, calcium fluoride or mixtures thereof in said feedstock so that said puffing inhibitor is present during the coking operation.

2. A process according to claim 1, characterized by the fact that the puffing inhibitor is added to the feedstock in the form of a predispersed liquid concentrated dispersion of said puffing inhibitor in a liquid medium compatible with said feedstock.

3. A process according to claims 1 or 2, characterized by the fact that the puffing inhibitor used has a particle size diameter such that 100% of said particles are less than 5 microns and 70% are less than 2 microns.

4. A process according to any one of the preceding claims, characterized by the fact that the puffing inhibitor is dispersed in a portion of the coker feedstock.

Revendications

1. Un procédé pour la production de coke aciculaire non-gonflant ayant une caractéristique CTE de graphite de pas plus de $7 \times 10^{-7}/°C$ dans l'intervalle de 0° à 50°C utilisable pour transformation en graphite de la qualité pour électrodes par cokéfaction retardée de charges de pétrole ayant une teneur en soufre combiné moléculairement dans des constituants de cette charge suffisamment élevée pour contribuer à une dilatation volumétrique irréversible lors du chauffage à une température de 1400°C ou plus, en présence d'un inhibiteur de gonflement, caractérisé par la dispersion de 0,05 à 0,5 % en poids d'un inhibiteur de gonflement qui est de l'oxyde de fer, du fluorure de calcium ou leurs mélanges dans la charge de manière que cet inhibiteur de gonflement soit présent dans l'opération de cokéfaction.

2. Un procédé selon la revendication 1, caractérisé par le fait que l'inhibiteur de gonflement est ajouté à la charge sous la forme d'une dispersion concentrée liquide prédispersée de cet inhibiteur de gonflement dans un milieu liquide compatible avec la charge.

3. Un procédé selon les revendications 1 ou 2, caractérisé par la fait que l'inhibiteur de gonflement utilisé a une granulométrie telle que 100 % des particules aient moins de 5 micromètres de diamètre et 70 % moins de 2 micromètres.

4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé par le fait que l'inhibiteur de gonflement est dispersé dans une portion de la charge de l'unité de cokéfaction.

Patentansprüche

1. Verfahren zum Erzeugen eines in Graphit von Elektrodenqualität umwandelbaren, nicht-blähenden Nadelkokses mit einem Graphit-Wärmeausdehnungskoeffizienten von höchstens $7 \times 10^{-7}/°C$ im Bereich von 0°C bis 50°C, in dem ein von Erdöl abgeleitetes Ausgangsmaterial, das in Komponenten des Ausgangsmaterials so viel molekular gebundenen Schwefel enthält, daß er bei einer Erhitzung auf eine Temperatur von oder über 1400°C zu einer nichtumkehrbaren volumetrischen

Expansion beiträgt, in Anwesenheit eines blähungshemmenden Mittels einer halbkontinuierlichen Verkoksung unterworfen wird, dadurch gekennzeichnet, daß in dem Ausgangsmaterial 0,05 bis 0.5 Gew.% des aus Eisen, Calciumfluorid oder Gemischen derselben bestehenden, blähungshemmenden Mittels dispergiert werden, so daß das blähungshemmende Mittel während des Verkokens vorhanden ist.

2. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das blähungshemmende Mittel zu dem Ausgangsmaterial in Form einer vordispergierten, konzentrierten flüssigen Dispersion des blähungshemmenden Mittels in einem mit dem Ausgangsmaterial verträglichen, flüssigen Medium zugesetzt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das verwendete blähungshemmende Mittel einen solchen Teilchendurchmesser hat, daß 100% der Teilchen kleiner sind als 5 um und daß 70% kleiner sind als 2 um.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das blähungshemmende Mittel in einem Teil des zu verkokenden Ausgangsmaterials dispergiert wird.
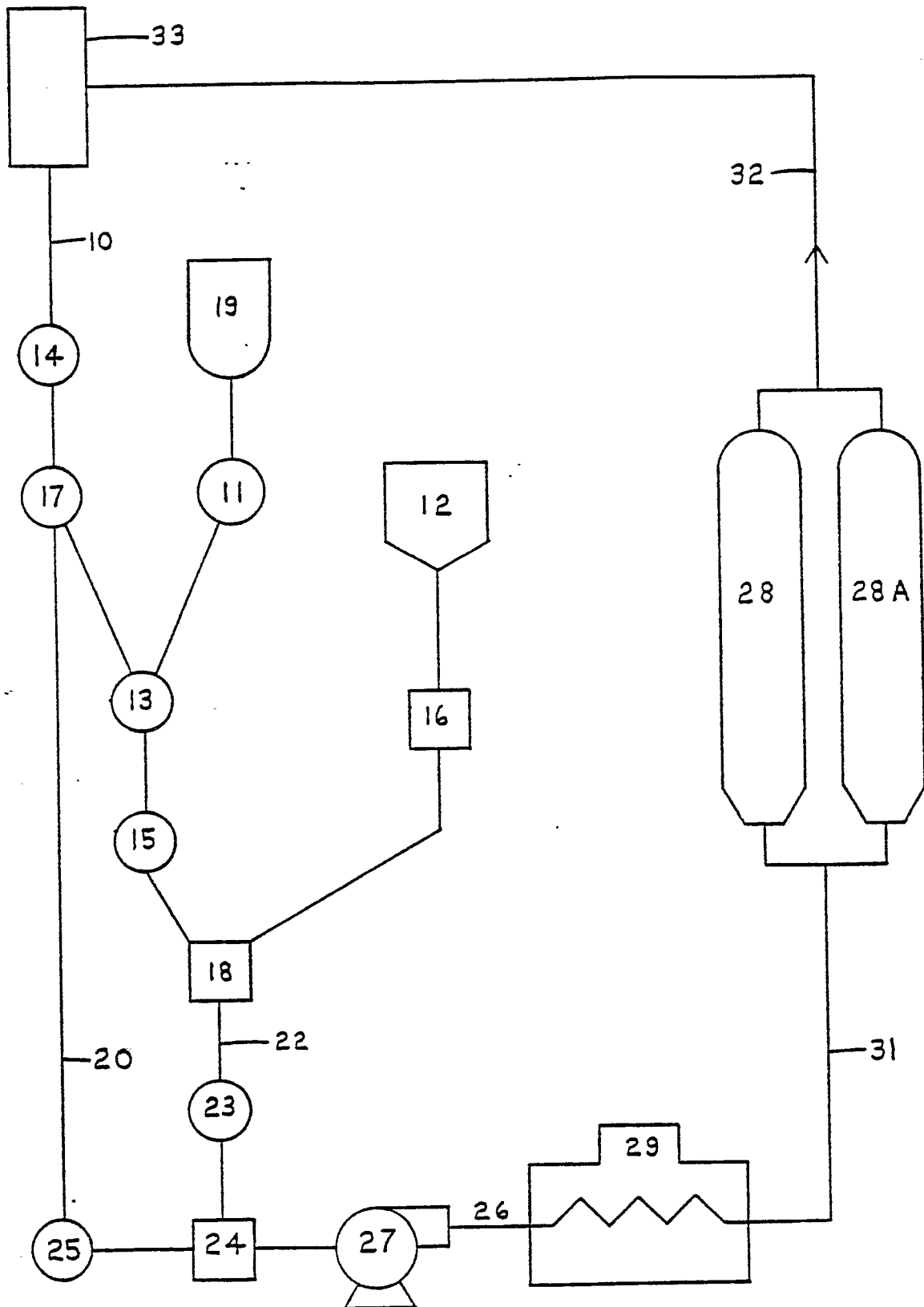
FIG. 1.