

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 245 814
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87106786.4

(51) Int. Cl. 4: C10K 1/06

(22) Date of filing: 11.05.87

(30) Priority: 14.05.86 IT 1247686

(43) Date of publication of application:
19.11.87 Bulletin 87/47(84) Designated Contracting States:
AT BE CH DE ES FR GB GR LI LU NL SE

(71) Applicant: **ITALIMPIANTI Società Italiana**
Impianti p.a.
Piazza Piccapietra, 9
I-16121 Genova(IT)

Applicant: **NUOVA ITALSIDER SpA**
Via Corsica n.4
I-16128 Genova(IT)

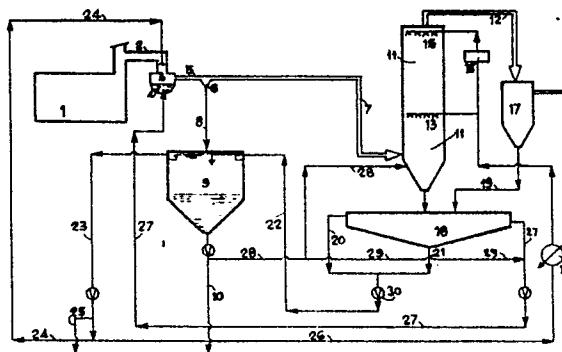
(72) Inventor: **Proface, Emanuele**
Via Bonifacio 2/21
I-16142 Genova(IT)
Inventor: **Pascale, Nicola**
Via Chiacchio 4
I-80028 Grumo Nevano (NA)(IT)

(74) Representative: **Porsia, Bruno et al**
c/o Succ. Ing. Fischetti & Weber Via Caffaro
3/2
I-16124 Genova(IT)

(54) **Cooling, dehumidifying, de-naphthenizing and detarring plant for coal distillation gases.**

(57) The process and respective plant are designed to process the gas distilled out of coal and exiting from coke-ovens (1), through a first cooling step down to 80-85°C, by means of water sprays, thus obtaining a partial condensation of tar and naphthalene which will be collected in a manifold-tank or header (3) together with the cooling water and steam condensate. Thereafter, the gas is separated from the condensed materials and is then further cooled in a water-spray tower (11) down to a temperature of 2-30°C to cause the total condensation of tar and almost total condensation of naphthalene and steam, thus purifying the gas from said materials. Naphthalene is removed from the cooling water and condensate flowing out of said tower (11) by absorbing it completely into the tar which is also contained in said water, by processing said water in a suitable decantation and flotation tank (18) where tar will settle down and naphthalene will float. Tar and naphthalene will be removed through suitable ducts (20,21) from the bottom and surface, respectively,

and then introduced into a single piping (22) where they will contact with each other and tar will absorb naphthalene by dissolving it. Water from various sections of the plant will collect in a decanter (9) where the tar that has absorbed naphthalene settles down and is removed, whilst the purified water is recycled. Suitable provisions are utilized to promote and to accelerate to a maximum extent the absorption of naphthalene into the tar, during all the steps of the process.



"Cooling, dehumidifying, de-naphthenizing and de-tarring plant for coal distillation gases"

The gas which is produced in coal-distilling plants contains - when flowing out of the distilling banks - steam, tar, naphthalene, anthracene oils, ammonia, raw benzol, hydrogen sulphide, and traces of other chemicals.

Some of these substances are recovered from said gas as by-products suitable for usage and, therefore, for sale. Tar, naphthalene and ammonia must be removed from said gas because, when cooled in the distribution piping, these substances will condense together with steam and cause serious fouling and corrosion problems within said piping networks. In the past, these substances were removed from the gas to be used as by-products, but nowadays they are manufactured through other, more economical processes; therefore, their removal from said gas is effected, substantially, to solve the problems mentioned above.

For this purpose, gas flowing out of the distilling banks is passed through a succession of apparatuses designed to remove both recoverable and undesired substances from said gas.

Gas flowing out of each distilling oven is conveyed into a header or manifold where the gas from all the banks is collected. In the downflow end-portion of the pipes conveying the gas from said ovens to said header, water is sprayed to lower the temperature of the gas to 80-85°C. The condensation is thus obtained of steam, of most tar and anthracene oils, and of a small fraction of naphthalene, which will collect in the header together with said gas. Naphthalene is absorbed by dissolving it in the tar and anthracene oils.

Gas, water, tar and anthracene oils flow together out of said header and are conveyed through a suitable piping to a separator to separate said gas therefrom. Water, tar and anthracene oils, after separation from said gas, are conveyed to a decanter where said tar and anthracene oils will settle down onto the bottom to be then removed, and water is re-cycled.

The gas passing beyond said separator still contains all the by-products mentioned above, including the fractions of tar, anthracene oils and naphthalene that have not condensed during said cooling step.

In the immediately successive step, the gas is purified by removal of the remaining tar and naphthalene therefrom.

In the heretofore known plants, this fraction of naphthalene is removed together with all the remaining tar. For this purpose, said gas is scrubbed in water-cooling towers, where it is cooled to a temperature of 25 to 35°C, thus obtaining the complete condensation of tar and of a fraction of naph-

thalene that has been dissolved in said tar. Tar is then separated from the water in a suitable decanter. The remaining naphthalene is then removed from the gas in a scrubbing plant by means of suitable solvents, usually anthracene oils or automotive diesel oil. If anthracene oils are used, an oil-regenerating system is required, since said oils are quite expensive. The use of diesel oil requires no regenerating system, since it may be used as a fuel because the naphthalene therein causes no combustion trouble. However, the use of diesel oil as a fuel involves an increase of costs in the combustion systems, because it is substituted for the less expensive coke-oven gas.

The plant of the present invention, in addition to the cooling and de-humidification of said gas, and to the complete removal of tar therefrom, enables the elimination of naphthalene from said gas with no need of solvents, such as oils or diesel oil, with resulting economy due to the lower capital and running costs - in that no regeneration of said oils is required and diesel oil need not be substituted for the less expensive coke-oven gas - and to the lower maintenance costs.

In the plant according to the invention, the gas flowing out of said header and having a temperature of 80-85°C is scrubbed and cooled by means of atomized water in a cooler wherein the scrubbing water has a temperature slightly above 0°C, usually about 10°C. The gas, passing through the cooler in countercurrent, i.e. from the bottom upwards, contacts said cooling water - which is atomized into very fine droplets and, therefore, has a very large heat-exchange surface - and is cooled thereby so as to give off its steam in excess at that temperature (said steam being then condensed), its residual tar, and the vapors of the aromatic hydrocarbons therein, mainly naphthalene, which will be also condensed due to said low temperature.

The gas flowing out of the top of the cooler, may still contain residual droplets of water, particles of tar and naphthalene either incorporated or not in said droplets of water and to be removed in a successive cyclone separator or any other suitable separator, such as electrostatic filters, Venturi tubes, etc. Upon exiting from these devices, said gas is thoroughly devoid of tar and only contains the amount of gaseous naphthalene to saturate said gas at its post-cooling temperature. Thereafter, said gas is passed through the successive purifying and processing systems, just like in the conventional plants.

The scrubbing water flowing out of the cooling system contains a much higher rate of naphthalene than the water flowing out of the known plants, due to the lower cooling temperature, which has caused a much higher condensation of naphthalene.

Therefore, the problem of removing naphthalene for the scrubbing water is more serious than in the known plants. In the latter, naphthalene is absorbed by tar during the intimate contact therebetween and due to the solubility of naphthalene in tar and to the small amount which is found dissolved in the latter, usually about 5%. In the plant of the present invention, the amount of naphthalene to be eliminated is much higher due to the lower cooling temperatures of gas; therefore, special and new provisions have been used therein to enhance the contact between tar and naphthalene, whereby the latter may be absorbed thoroughly by dissolution in the tar.

For this purpose, the scrubbing water exiting from the cooler is conveyed into a flotation and decantation tank, where the materials lighter than water - such as naphthalene flakes and foams, light oils, etc. - will float, and the heavier materials - such as tar, anthracene oils, etc. - will settle down.

It is to be noted that the latter materials have already absorbed a fraction of naphthalene in the cooler, in the piping to the tank and in the tank itself, due to the intimate contact between naphthalene and tar therein.

The floating materials including naphthalene, are removed by suction from the surface of the scrubbing water in the tank, and the settled materials, mostly tar, are sucked from the bottom. Both of them, once sucked away, together with some of the water, are conveyed into a single piping where they are mixed into intimate contact with each other, which is enhanced by the turbulence caused by the pumping devices and the speed of the fluid, which is purposely maintained at suitable values.

Therefore, the tar will absorb the naphthalene during the travel thereof through said piping, the latter having such a length whereby almost all the free naphthalene will be absorbed at the outlet thereof.

Said piping then discharges water and tar, that has absorbed most of the naphthalene, into the decanter which also receives the water deprived of gas in the separator following said header, the absorption of the still free residual naphthalene by the tar being continued in said decanter. The tar is then allowed to settle down in said decanter and is discharged, while the water, now devoid of tar and naphthalene, is re-cycled.

A small fraction of the water reaching the decantation and flotation tank from the cooler and separator, as described above, is sucked together with the materials either floating on the surface and

settled on the bottom, while the remaining water is discharged through a piping arranged at about an intermediate level of the decantation and flotation tank. Such water contains small particles of naphthalene which have not yet reached the surface owing to their small buoyancy resulting from their very small dimensions. Such water is conveyed to said header and introduced at the bottom thereof, where it mixes with the water being sprayed for the first cooling of the gas and with the water that condenses therein, which is rich of tar having a low content of naphthalene because the latter, due to the high temperature therein, has only condensed to a maximum extent. Therefore, naphthalene will be dissolved easily and completely in the tar it contacts within said header and successively within the following piping, within the separator and finally in the tar decanter.

The summation of the absorbing actions of tar in the several sections of the plant in the manner described above ensures the complete removal of naphthalene from the ammoniacal cooling water; at the same time, the gas flowing out of the cyclone arranged downstream of the cooler is completely devoid of tar and it only contains the amount of naphthalene determined by the saturation of the gas at the temperature it has been cooled, in a percentage which is completely satisfactory as far as the cleanness of the distribution network is concerned.

The degree of purification of gas from naphthalene depends upon the average temperature of said gas in the piping of the distribution network, because said temperature controls its condensation to the dew point thereof, with attendant fouling and clogging problems. In the countries where the ambient temperature is higher, higher percentages of naphthalene in the gas may be tolerated than in colder countries. This affects the selection of the various cooling temperatures for the gas, and of all the parameters affecting the greater or smaller extent of contact between tar and naphthalene such as to avoid any condensation within the gas distribution piping. These parameters may be varied in the same plant, from time to time, depending on the ambient temperatures, thus saving energy when the ambient temperature permits a higher concentration of naphthalene in the gas.

The naphthalene that has been removed from the gas is incorporated in the tar, and the latter may be used with no purification, for example, as a fuel. Should a purification of the tar be required for other utilizations, no additional costs are involved with respect to the known plants, because the tar produced in the latter also contains a percentage of

naphthalene, usually about 5% as stated above, and the higher concentration thereof in the tar produced in the plant of the invention requires no particular plants and processes.

With the plant according to the invention, the recovery of naphthalene, if desired, has a lower cost than with the purification systems heretofore known, because the entire recovery would be effected by distillation of only the tar.

With reference to the drawings, an embodiment of the invention will be described as an illustrating and not-limiting example.

The gas flows out of the banks of coke-ovens, only one of which is shown in the drawing for simplicity's sake and is indicated at 1, and is conveyed to the header 3 through the piping 2. In the end portion of the piping 2 adjacent said header, suitable water sprays will lower the temperature of the gas to 80-85°C. Due to this cooling action, the excess steam in the gas flowing out of said bank is condensed and will collect into the bottom 4 of the header 3 together with the water that has been used for cooling purposes.

Said cooling of the gas will cause as well the condensation of most of the tar, which will also settle down to the bottom of the header 3, and of a small fraction of naphthalene that will be absorbed by the tar.

Water, tar and gas will be conveyed into a piping 5 to reach a water-gas separator 6 where the gas is separated from the tar-containing water.

The gas pursues its travel in the piping 7, and water and tar are conveyed through the piping 8 into a decanter 9, where the tar will settle down onto the bottom due to its greater specific gravity with respect to water. The tar on the bottom of the decanter is discharged through a pipin 10 and is recovered.

The gas passing through the piping 7, deprived of most tar and at a temperature of 80-85°C, enters the lower portion of a spray-cooler 11. It moves upwards through the entire tower cooler 11 and is discharged from the top thereof through the piping 12.

Within the tower cooler, cold water is sprayed in a finely atomized condition. The gas moving upwards in countercurrent with the finely atomized droplets falling down by gravity meets a first set of spray nozzles 13 for atomizing water usually at about 25-30°C which is cooled, for example, by means of sea water through heat-exchangers 14, and thereafter a second set of spray nozzles 15 for atomizing water at a temperature of 2-10°C which is cooled, for example, by means of refrigerating units 16.

The gas in the cooler 11 is cooled to a temperature which is a few degrees above the temperature of the cooling water, such as to 15°C if the temperature of the water is 10°C. During this cooling step, all the tar and most of the naphthalene are condensed. Tar and naphthalene, swept down by the water, fall down onto the bottom of the tower together with the cooling water and the condensate of steam still contained in the gas, excepted those very fine particles that may be swept along by said gas. This gas is then conveyed to the droplet remover 17 where it is deprived of those particles.

The refrigerating unit for the final cooling of the gas in the tower is regulated so as to minimize the energy consumption. If the gas is cooled to the temperature of 15°C, the amount of gaseous naphthalene in the gas is 0.25 g/Nm³, which amount generally causes no fouling problem in the pipes even if the temperature of the gas flowing through the network falls some degrees below said temperature. If the average temperatures in the pipes are above 15°C, the gas need not be cooled to said temperature, since naphthalene will not condense at all. Said possibility of regulating this unit allows a remarkable saving either of electric power required for operating the refrigerating unit if the latter is of the compression type, or of vapor if it is of the absorption type.

The water that collects on the bottom of the cooler 11 is conveyed through the piping 17 into a decantation-flotation tank 18, where the water that is captured in the cyclone 17 is also conveyed through the piping 19.

In the decantation-flotation tank 18, the materials lighter than water, such as naphthalene flakes and foams, will float and the heavier materials, such as tar and anthracene oils, will settle onto the bottom. The floating materials are removed from the surface through the piping 20, and the settled materials are removed from the bottom through the piping 21.

The two pipings 20 and 21 lead to a single piping 22 which conveys to the decanter 9 the mixture of tar, naphthalene and water being sucked together.

During the travel from the decantation-flotation tank 18 to the decanter 9, tar and naphthalene are closely in contact with each other, which is enhanced by the turbulence caused by the pump 30 and the speed of the fluid in the piping, said speed being maintained at suitable values. The length of the piping 22, moreover, is such as to permit a nearly complete absorption of naphthalene into the tar. It is to be noted that, partially, such an absorp-

tion has occurred in the tower, during the cooling step, in the cyclone, in the piping conveying the fluids into the decanter, and said absorption is completed in said decanter.

The ammoniacal water being removed from the surface in the decanter 9, therefore, is devoid of tar, which has all settled down onto the bottom, and of naphthalene, which has been completely absorbed by the tar.

Said water is re-cycled, and a fraction of it will be used for the first cooling step in the header, to which it is conveyed through the pipings 23, 24 and from which it resumes the cycle described above. The remaining fraction of the water from the decanter 9 is conveyed to the cooling tower through the piping 26. It is first cooled by means of cooling water in the heat exchanger unit 14 to a temperature of about 25-30°C and it is partly sprayed through the nozzles 13 in the cooler, while the remaining portion is further cooled in the refrigerating unit 16 and is sprayed in said cooler through the nozzles 15. Not all the water deprived of tar and naphthalene is re-cycled, because during the process it joints with the condensation water and it grows rich with ammonia, whereby a portion thereof is drawn off and is conveyed to the ammonia distilling plant through the piping 25.

A certain amount of water supplied to the decantation-flotation tank 18 by the cooler 11 and cyclone 17, is withdrawn through the pipings 20 and 21 together with tar and naphthalene, as stated above, but most of it is withdrawn at an intermediate level of the decantation-flotation tank through the piping 27. This water contains suspended therein very fine particles of tar and naphthalene such that they have not been able to move up to the surface or down to the bottom of the decantation-flotation tank. Said water is conveyed through the piping 27 to the bottom of the header 3. During this travel a fraction of the naphthalene is absorbed by the tar, and the remaining fraction will join, on the bottom of said header, the freshly condensed tar, which has a low naphthalene content. Therefore, this tar absorbs in the header said remaining naphthalene almost completely, whereafter it will pursue the absorption steps described above during the successive travel.

The amount of tar may not be enough, in certain sections of the plant, to absorb, with sufficient rapidity, the condensed naphthalene in that section. Therefore, some tar is drawn off the sections where it is not saturated with naphthalene or, preferably, where it has a relatively low content of naphthalene, and is conveyed to other sections where naphthalene is to be absorbed. In the illustrated example, a piping 28 is provided to withdraw tar from the bottom of the decanter 9 and to convey it to the bottom of the cooler 11 and,

through a branch 29, into the piping 27. In fact, in these sections the existing amount of tar or the naphthalene-saturated condition of tar are such as to either nullify the absorption of free naphthalene, or to permit it with insufficient rapidity.

Claims

1. A cooling, dehumidifying, de-naphthenizing and de-tarring process for coal distillation gas exiting from coke-ovens (1), wherein:

-said gas is cooled from the temperature of 700-900°C it has upon exiting from the coke-ovens (1) to a temperature of 80-90°C, by means of water sprays at the temperature of about 60-70°C within the end, vertical portion of each of the pipes (2) leading the gas from an oven (1) to the header (3) where all the gas from a bank is collected so as to condense the steam exceeding the saturation degree at that temperature and to condense most tar and anthracene oils which collect in said header (3) together with the cooling water being sprayed, and a small fraction of naphthalene which dissolves in the tar and anthracene oils;

-said gas then flows out of said header (3) into the pipings, drawing along water, tar and anthracene oils to a water/gas separator (6), wherein said gas is separated from said other materials, and the latter are then collected in a decanter (9);

-tar and anthracene oils settle down by gravity onto the bottom of the decanter (9), whereby the water, so deprived of tar and anthracene oils, may be re-used for the process;

-said gas then proceeds beyond the separator (6), still at the temperature of 80-90°C, to a cooler (11), usually of the cold water spray type, wherein water at the temperature of 2-30°C is sprayed to cool the gas to a temperature of a few degrees above that of the water, so as to achieve the condensation of all the tar and naphthalene, corresponding to the saturation thereof, which will be conveyed to a decantation-flotation tank (18) together with the water that has been sprayed and that has been condensed as a result of said reduction of temperature;

-said gas then proceeds to a droplet separator (17) where the remaining very fine particles of water, tar and naphthalene, the latter two being either incorporated or not in said droplets, are separated and conveyed to said decantation-flotation tank (18);

-said gas, so deprived of naphthalene and tar then enters the outlet pipings of the plant to be further processed or to be utilized;

-the amounts of water containing tar and naphthalene, which are conveyed into the decantation-flotation tank (18) from the cooler (11) and droplet separator (17) will dwell therein to permit the particles lighter than water, substantially naphthalene, to float up to the surface, and to permit the heavier particles, i.e. tar, to settle down onto the bottom, and said water is then withdrawn from an area about at an intermediate level of the decantation-flotation tank (18) and it only contains particles which have remained suspended therein due to their very small dimensions;

-said water is then conveyed into the bottom of said header (3), where the flows of gas from the distilling ovens collect together, and joins the cooling water and condensation water containing the condensed tar;

-the naphthalene that is condensed in the cooler (11) and is collected in the droplet separator (17) contacts with the condensed tar and is absorbed thereby by dissolution, said absorption occurring successively in the cooler (11) and in the droplet separator (17), in the piping leading to the decantation-flotation tank (18), within said decantation-flotation tank (18), in the piping (27) from the latter to said header (3); within the header where it contacts the freshly-condensed tar, in the successive piping (5) from the header (3) to the water/gas separator (6), in the following piping (8) from the separator (6) to the decanter (9) of tar, and finally into said decanter (9), where the absorption of naphthalene into the tar is completed;

-the naphthalene that has moved up to the surface in the decantation-flotation tank (18) and the tar that has settled down onto the bottom thereof are removed through surface skimming and bottom discharging pipes (20,21), respectively, together with a certain amount of water, and are conveyed together in a single piping (22) to the tar decanter (9);

-during the travel from the decantation-flotation tank (18) to the tar decanter (9), naphthalene and tar contact intimately with each other, whereby naphthalene will be absorbed by tar, the absorption being then pursued in the decanter (9) until it has been completed;

-the water recovered in the decanter (9) and now deprived of naphthalene and tar is partly re-used for the process of the invention.

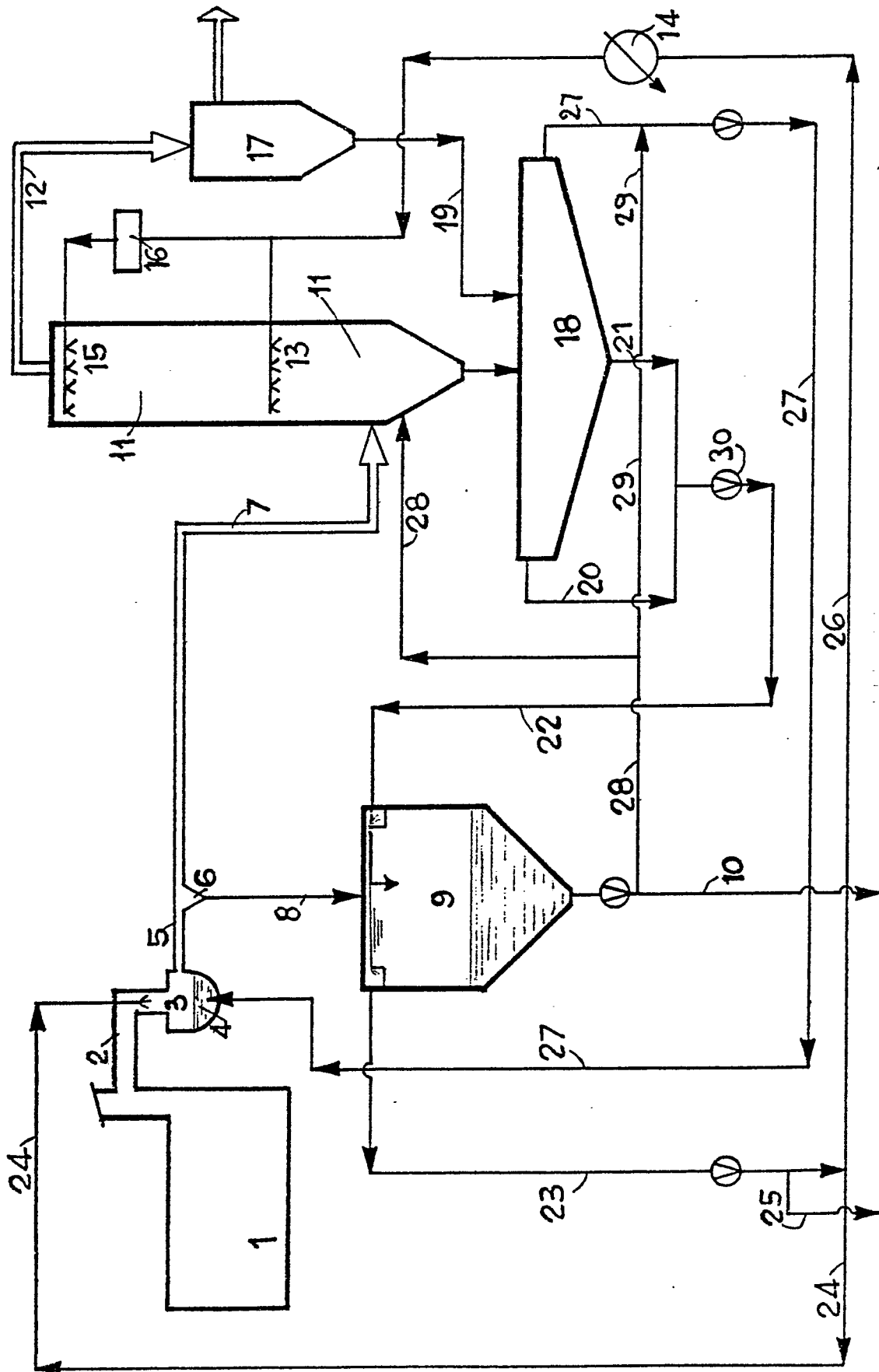
2. A process according to claim 1, wherein the gas being cooled in said cooler (11) is first acted upon by sprayed water (13) at a temperature of 25-30°C and then by sprayed water (15) at a temperature of 2-10°C.

3. A process according to claims 1 and 2, wherein the water (13) being sprayed at a temperature of 25-30°C is cooled in heat exchangers by means of cooling water naturally available at a slightly lower temperature, and the water (15) being sprayed at 2-10°C is cooled by means of refrigerating units (16) which, in turn, are cooled by means of said available water.

4. A process according to claim 1 either alone or in combination with one or more of the claims 2 to 4, wherein the lower temperature of the cooling water being sprayed in the cooler (11) is above 10°C, up to 30°C, and said gas is cooled only few degrees below the ambient temperature in the space where said gas is distributed, or at the same temperature.

5. A process according to claim 1 either alone or in combination with one or all the claims 2 to 4, wherein some of the tar that in certain steps of the process is not yet saturated with naphthalene, or preferably has a low content of naphthalene, is drawn off where such conditions occur and, through suitable pipings, is conveyed to other steps of the process, which lack of tar capable of absorbing readily the naphthalene thereat, so as to enhance the contact between naphthalene and said unsaturated tar and thus to accelerate the absorption of naphthalene into said tar.

6. A process according to claim 1 either alone or in combination with one or more of the claims 2 to 5, wherein more or less strong turbulent movements are created within the pipings of the plant by acting either on the speed of the fluids, or the characteristics of the pumps, or the configuration of the pipings, or the like, so as to enhance the contact between tar and naphthalene and thus to accelerate to a maximum extent the absorption of naphthalene into the tar.





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-3 451 896 (SCHÖN) * Column 5, line 1 - column 6, line 14; figure 1 *	1-6	C 10 K 1/06
Y	--- US-A-4 239 511 (AUSTERMÜHLE) * Claims 1-9 *	1-6	
A	--- FR-A-2 358 459 (OTTO & CO.) * Claims 1-3 * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 K C 10 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-08-1987	Examiner MEERTENS J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			