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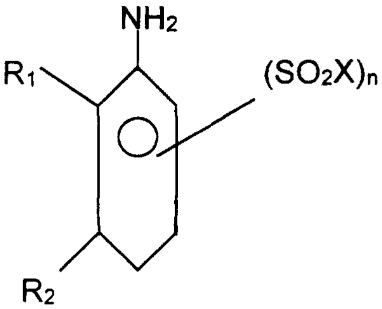
(54) A method for the anti-fouling treatment in petrochemical plants

(57) A method for the anti-fouling treatment in petrochemical plants is described, which comprises the washing of hydrocarbons, contaminated by carbonyl compounds, with an alkaline solution comprising an effective amount of a compound according to the general formula (I) as follows:

(I)



in which X= H, NH_2

n= 0 or positive integer number
R_1, R_2, being equal or different from each other, are H, linear, branched or cyclic aliphatic chain C_1-C_{10}, or R_1 and R_2 are joined together to form an aromatic cycle, substituted with the $(SO_2X)_n$ group if necessary

taking care that at least one $(SO_2X)_n$ group is always present in the molecule and with the exclusion of 4-aminobenzenesulphonic acid; the corresponding salts of formula (I) compounds and the corresponding mixtures.

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Description

Field of the invention

[0001] The present invention concerns a method for the anti-fouling treatment in petrochemical plants. In particular, the anti-fouling treatment is carried out in an aqueous alkaline environment.

Background art

[0002] According to the present invention, the term fouling means the fouling of the surfaces which come into contact with fluids during the treatment of hydrocarbons in general, especially the production of olefin compounds. More particularly, in the pyrolytic cracking of hydrocarbons, significant amounts of other compounds are formed namely, among others, H_2S, organic acids, aldehydes and ketones in addition to the olefin compounds of interest. Stages of alkaline washing are possible to eliminate these contaminants, for instance with soda solutions, to remove the acidic substances. However, in these conditions the carbonyl compounds polymerize and/or form condensation products which deposit on and therefore dirty the surfaces of the plant itself. Many attempts have been made to minimize said fouling, essentially based on the use of amine compounds. For instance, US 5.264.114 describes a procedure in which aliphatic and aromatic amines are used; however some of them are scarcely soluble in the aqueous medium used for the anti-fouling treatment. EP 824.142 selects a series of aromatic amines on the bases of their solubilization in the aqueous treatment medium. The tests carried out are only indicative and the sodium salt of 4-aminobenzenesulphonic acid is especially preferred, not so much considering its anti-fouling activity as its better solubility in water as regards the other disclosed products, activity being equal. Besides, the tests illustrated are laboratory tests, not easy to transfer into plant reality, therefore the real effectiveness of the products has not really been tested.

[0003] It has now been found that a class of compounds, which are used in the dye industry, is particularly suitable and gives high yields in the anti-fouling treatment of petrochemical plants.

Field of the Invention

[0004] It is an object of the present invention a method for the anti-fouling treatment in petrochemical plants, in which fouling is caused by the presence of carbonyl compounds, said method comprising a washing stage with an alkaline solution containing an effective amount of a compound having the structural formula (I) as in claim 1. In particular, the compound can be a naphthalenesulphonamine and the corresponding salts, an aminonaphthalenesulphonamide, an aminobenzenesulphonamide and the corresponding mixtures of the aforesaid compounds.

[0005] Another object of the invention is the use of the formula (I) compounds to carry out the method according to the invention.

[0006] Further objects will be evident from the detailed description of the invention.

[0007] These objects are obtained by means of a method and a use according to the enclosed claims.

Brief description of the figures

[0008] Fig. 1 is a graph of spectrophotometric measurements at 450 nm.

[0009] Fig. 2 is a graph of spectrophotometric measurements at 500 nm

[0010] Fig. 3 is a graph of spectrophotometric turbidimetry measurements at 720 nm, turbidity tendency during the first twelve hours.

[0011] Fig. 4 is a graph of spectrophotometric turbidimetry measurements at 720 nm, turbidity tendency during the following twenty hours.

[0012] Fig. 5 shows a plant diagram for olefin production.

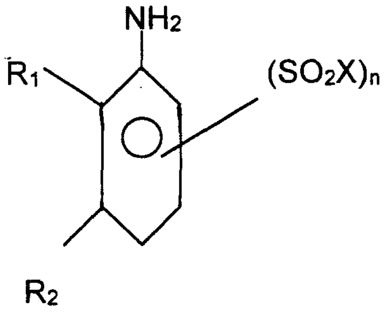
[0013] Fig. 6 shows a gas chromatogram related to example 3.

[0014] Fig. 7a- 7b show a molecular weight detector diagram related to example 3.

Detailed description of the invention

[0015] The present invention refers to a method to inhibit the formation of fouling deposits during the pyrolytic production of olefins starting from hydrocarbons. The olefins can be: etylene, propylene, butylenes, butadiene, etc., which are produced by the pyrolytic cracking of hydrocarbons. Such deposits, as said above, are formed due to the presence, in the acidic gases generated during the production of said olefins, of carbonyl compounds that polymerize and/or condense during the washing of said acid gases with alkaline solutions. Acetaldehyde is among the carbonyl compounds of interest. Such carbonyl compounds cause colouring, more or less intense, of the alkaline solutions depending on their concentration, that typically varies between 1 and 10,000 ppm. The colouring is produced by the formation of an adduct that precipates over time and deposits on the surfaces of the plant (fouling).

[0016] The alkaline washing process, according to the invention, includes treatment of the contaminated hydrocarbons with an alkaline solution comprising an effective amount of a compound according to the general formula (I) as follows:



(I)

[0017] In which X= H, NH_2

n= 0 or a positive integer number

R_1, R_2, being equal or different from each other, are H, linear, branched or cyclic aliphatic chain C_1-C_{10}, or R_1 and R_2 are joined together to form an aromatic cycle, substituted with the $(SO_2X)_n$ group, if necessary

taking care that at least one $(SO_2X)_n$ group is always present in the molecule and with the exclusion of 4-aminobenzenesulphonic acid.

[0018] The salts of formula (I) compounds and the corresponding mixtures also come within the scope of the present invention. The salts can be Na and/or K salts, in particular.

[0019] The solution to be used has a pH>7 and can be alkaline by the addition of basic substances, namely sodium and/or potassium hydroxides, amines. Hydroxides with a concentration of approx. 10% in weight are preferred. This solution is generally added to the plant area known as the washing tower of the cracking gas or alkaline scrubber within which the olefin products to be purified are carried. The scrubber preferably operates at room temperature.

[0020] The alkaline solution is recirculated several times in the washing tower and is considered unfit for further use when the olefin product contains too many contaminants. Such contaminants can be, in addition to the said polymerization and/or condensation products, of the carbonyl compounds that cause the aforesaid fouling, also benzene and its by-products and other aromatic hydrocarbons.

[0021] With reference to the compounds that produce fouling, these, depending on their concentration in the basic solution, cause a possible turbidity as well as a yellow colouring that gradually darkens until becoming red for concentrations of carbonyl compounds up to approx. 2000 ppm. For higher concentrations the red colour comes into a turbidity that progresses until changing into a proper precipitate. Therefore, normally the amount of carbonyl compounds is initially up to several tens of ppm, and collecting in the alkaline solution, their concentration can reach approx. 10,000 ppm.

[0022] In the case of high carbonyl compound concentrations, approx. >2000ppm, it is preferred to carry out the invention treatment by using a sulphanilamide according to the formula (I).

[0023] In the case of low carbonyl compound concentrations, approx. <2000ppm, the use of a naphthalenesulphonamine, according to the formula (I) or its sodium and/or potassium salt, is preferred.

[0024] According to the invention, the formula (I) compound is preferably added to the alkaline washing solution in order to obtain a molar ratio of active/carbonyl compound ranging between 1.0:1.0 to 1.0: 40.0 in the final solution, preferably from 1.0:1.0 to 1.0:10.0.

[0025] The formula (I) compounds, including 4-aminobenzenesulphonic acid and its salts, added to the alkaline solution, according to the invention method, proved particularly suitable not only in inhibiting fouling, but also in drastically reducing the amount of aromatic compounds present in the alkaline solutions.

[0026] In fact, it has been tested a drastic reduction in the amount of aromatics, particularly benzene and derivatives, which are solubilized or emulsified in the alkaline solutions coming out of the scrubber. Such solutions, at the end of the washing cycle, must be disposed of and the greater the amount of aromatics, the more serious the disposal problems. In fact, if the quantities of aromatics are too high, the biological disposal of them is impossible and one must resort to more drastic solutions, e.g. disposal by incineration.

[0027] The following examples are given to illustrate the invention and are not to be considered as limitative of the scope of the same.

EXAMPLES

[0028] The following expressions are used in the examples: E-4, MW, w/w respectively corresponding to: 10^{-4}, molecular weight, weight/weight. The compounds used were: Acetaldehyde (Sigma Aldrich reagent), Sodium Sulphanilate = sodium salt of 4-amino-benzenesulphonic acid (produced by Sorochimie), Sulphanilamide= 4-amine-benzene-sulphonamide (produced by Jamhik Dyechem Industries PVT Ltd.), Sodium Naphthalenesulphonate = sodium salt of 1-amine-naphthalene-4-sulphonic acid (produced by Rohan Dyes and Intermediates Ltd)

Example 1

[0029] The tests were carried out on 10 g solutions at 10% in weight of soda. Known equimolar amounts of the substances to be tested were added to them. In practice, 5.7 E-4 moles of each substance were added, corresponding to 0.11 g of Sodium Sulphanilate (MW 195- test tube 1 - 11000 ppm w/w), 0.10 g of Sulphanilamide (MW 172.21- test tube 2 - 10000 ppm w/w), 0.135 g of Sodium Naphthalene-sulphonate (MW 245.24 - test tube 3 - 13500 ppm w/w) and finally a test was done without adding any product (blank- test tube 0).

[0030] Fixed amounts of acetaldehyde, corresponding to 1.1 E-4 Moles, i.e. 4.8 mg (MW 44.054), were added to the test tubes. The additions were repeated five times, leaving about one hour between each addition: therefore, at the end of the test, a total amount of 24 mg/5.5 E-4 moles (i.e. 2400 ppm- w/w) of acetaldehyde was obtained in each test tube. The molar ratio obtained at the end between active compounds and acetaldehyde was therefore approx. 1:1.

[0031] Upon expiry of each hour, before the addition, the colour tendency of the various solutions was monitored, taking two spectrophotometric measurements at 450 nm (Fig. 1) and at 500 nm (Fig. 2), respectively, to highlight the tendency of the yellow and the red component.

[0032] Polymerization of the acetaldehyde was uncontrolled in the blank and strongly coloured the solution which proved decidedly less yellow in the test tubes in which the anti-polymerizing substances were present. The two graphs of Fig. 1 and Fig. 2 show the state of the absorbances:

[0033] The curves obtained at 450 nm as well as those at 500 nm confirm the better efficiency of Naphthalene-sulphonate on the Sulphanilamide which is, in any case, greater than the Sulphanilate.

Example 2

[0034] The operating conditions of example 2 were the same as those in example 1. In this case, 5.7 E-4 moles of each active compound were added, corresponding to 0.11 gr. of Sodium sulphanilate (MW 195- test tube 1 - 11000 ppm w/w), 0.10 g of Sulphanilamide (MW 172.21- test tube 2 - 10000 ppm w/w) and finally a test tube was kept without adding any product (blank- test tube 0).

[0035] In this case, a greater amount of acetaldehyde was added in order to induce the formation of a precipitate and therefore allow the turbidity measurement to be made.

[0036] In the series of test tubes in fact, a fixed addition of an amount of acetaldehyde corresponding to 2.2 E-4 Moles, i.e. 9.6 mg (MW 44.054) was carried out.

[0037] This addition was repeated eight times, leaving approx. one hour between each addition: therefore a total amount of 76.8 mg/17.4 E-4 moles (i.e. 7680 ppm- w/w) of acetaldehyde was obtained in each test tube. The molar ratio obtained at the end between products and acetaldehyde is therefore approx. 1:3.

[0038] Upon expiry of each hour, before the addition, the turbidity state-progress of the various solutions was monitored, taking spectrophotometric measurements at 720 nm.

[0039] After such additions, the solutions were left to rest for approx. 12 hours and then the turbidity was monitored: besides, without making any other additions, other measurements were carried out at approx. 4 hour intervals.

[0040] The first graph shows the turbidity tendency during the first twelve hours (and thus during the progressive additions).

[0041] The second graph instead shows the turbidity tendency over the following 20 hours, without the further addition of acetaldehyde.

[0042] The greater efficiency of Sulphanilamide, compared to Sodium Sulphanilate, particularly emerges in the second period, letting the added acetaldehyde polymerize: in this case, finding itself in conditions of high acetaldehyde concentration, the Sulphanilamide is the substance that shows the best protection against the formation of polymeric precipitates.

Example 3

[0043] An additive based on sodium 1-amine 4-naphthalenesulphonate is added to the caustic washing circuit in an olefine production plant in Italy.

[0044] The amount to be used is calculated on the bases of the amount of acetaldehyde arriving in the cracking gas: in particular, the ratio between sodium aminonaphthalene sulphonate and acetaldehyde is kept at approx. 0.3:1.

[0045] The entrainment of aromatic hydrocarbons, in general, and benzene in particular, in the exausted soda by the polymer formed from the condensation reactions of the base-catalysed carbonyls, was highlighted by running the plant for a period of time without treatment: the method herein below precisely allows the assessment of the benzene concentration during the caustic stage.

[0046] A method of benzene determination

[0047] An exact amount of sample is weighed and put in a separatory funnel: the amount of exausted soda necessary to carry out the method is estimated to be 4-500 gr.

[0048] The extraction is carried out with 20 ml of n-hexane: from the analyses made and the transparency estimation of the sodium solution after extraction, 4-5 extraction steps are sufficient.

[0049] The evaporation necessary to eliminate all the extracted polymers and isolate the light aromatic solvents (benzene and toluene), is done in successive steps:

T1 of the thermostatic bath= 50°C; Vacuum= 350 mbar; Time: 5 minutes
T2 of the thermostatic bath= 60°C; Vacuum= 250 mbar; Time: 10 minutes
T3 of the thermostatic bath= 70°C; Vacuum= 212 mbar; Time: 5 minutes

[0050] Having carried out the three evaporation steps of the sample, pure n-hexane was evaporated to eliminate any traces of benzene left on the cooling element. T of the thermostatic bath= 70°C; Vacuum= 350 mbar; Time: 5 minutes

[0051] All the evaporated substance was brought to 250 ml and analyzed by gaschromatographic means.

[0052] The method and the column used are listed as follows:

1. ULTRA1 HP column 25m x 0.20mm x 0.11μm;
2. He carrier flow: 2mL/min;
3. split 40:1;
4. T inj= 250°C;
T det.= 280°C.

[0053] The temperature ramp used is:

35°C for 8 min;
from 35°C to 150°C with 5°C/min;
from 150°C to 300°C with 25°C/min;
to 300°C for 3 min.

[0054] Fig. 6 shows one of the gas chromatograms obtained, with the benzene peak at 3.29 min. retention time (and identification of the same using a molecular weight detector - Fig. 7a- 7b- Hewlett Packard mod. HP5890)

[0055] The results obtained carrying out a series of analyses on the plant of Fig. 5, are shown in tables 1 and 2: table 1 illustrates the measurements obtained with the plant running at low load (one production line only), with and without treatment.

[0056] Table 2 shows the data obtained in the same plant, running at full load (two production lines) once again in the absence and, subsequently, in the presence of treatment.

Table 1

Conc. of benzene (ppm) without treatment
230
450
480
370
340
Conc. of benzene (ppm) with treatment
36
48
72
52
38

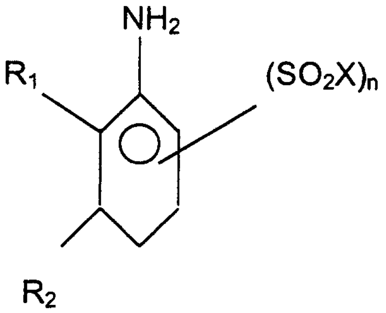
Table 2

Conc. of benzene (ppm) without treatment
530
1340
1830
860
1440
Conc. of benzene (ppm) with treatment
112
86
78
58
98

[0057] The data obtained clearly show the effect of the additive, according to the invention, as an anti-pollution product, with the important capacity of considerably limiting the presence of a carcinogenic substance, such as benzene in the exausted soda, regularly sent, in ethylene production plants, to the disposal plant of the refluent waters. The effect achieved is the important lowering of the ecological impact of the caustic solutions deriving from the washing towers of the cracking gases.

Claims

1. A method for the anti-fouling treatment in petrochemical plants comprising a washing of hydrocarbons, contaminated by carbonyl compounds, with an alkaline solution comprising an effective amount of a compound according to the general formula (I) as follows:



(I)

in which X= H, NH_2

n= 0 or positive integer number
R_1, R_2, being equal or different from each other, are H, linear, branched or cyclic aliphatic chain C_1-C_{10}, or R_1 and R_2 are joined together to form an aromatic cycle, substituted with the $(SO_2X)_n$ group if necessary
taking care that at least one $(SO_2X)_n$ group is always present in the molecule and with the exclusion of 4-aminobenzenesulphonic acid; the corresponding salts of formula (I) compounds and the corresponding mixtures.

2. A method as in claim 1 in which the salts are salts of Na and/or K.

3. A method as in claims 1-2 in which the solution is alkaline due to the addition of sodium and/or potassium hydroxides with a concentration of approx. 10% in weight.

4. A method as in claims 1-3 in which the solution is added to the washing tower of the cracking gas within which are carried the olefin products to be purified.

5. A method as in claim 4 in which the alkaline solution is recirculated several times in the washing tower.

6. A method as in claims 1-5 in which the formula (I) compound is added to the alkaline solution in order to give a molar ratio of active/carbonyl compound in the final solution which varies from 1.0: 1.0 to 1.0: 40.0.

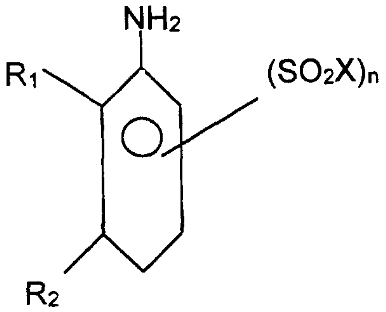
7. A method as in claim 6 in which the molar ratio varies from 1.0:1.0 to 1.0: 10.0.

8. A method as in claims 1-7 in which the compound is a sulphanilamide.

9. A method as in claims 1-7 in which the compound is a naphthalenesulphonamine or one of its sodium and/or potassium salts.

10. A method for the breaking down of aromatic hydrocarbons present in the aqueous solutions arising from the alkaline washing of hydrocarbons treated with pyrolytic cracking, said method comprising the stage of adding, to said alkaline solution, an effective amount of a compound according to the general formula (I) as follows:

(I)



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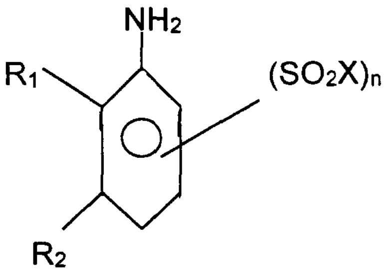
11. A method as in claim 10 in which the compound is a sulphanilamide.

12. A method as in claim 10 in which the compound is a naphthalenesulphonamine or one of its sodium and/or potassium salts.

13. A method as in claim 10 in which the compound is aminobenzenesulphonic acid.

14. The use of formula (I) compounds for the anti-fouling treatment in petrochemical plants:

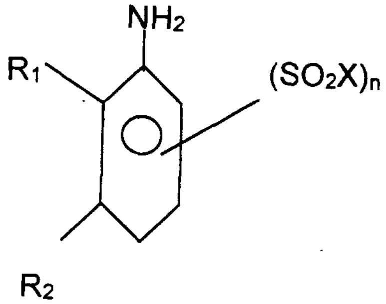


(I)

in which X= H, NH_2

n= 0 or positive integer number
R_1, R_2, being equal or different from each other, are H, linear, branched or cyclic aliphatic chain C_1-C_{10}, or R_1 and R_2 are joined together to form an aromatic cycle, substituted with the $(SO_2X)_n$ group, if necessary taking care that at least one $(SO_2X)_n$ group is always present in the molecule and with the exclusion of 4-aminobenzenesulphonic acid; the corresponding salts of the formula (I) compounds and the corresponding mixtures.

15. The use of formula (I) compounds for the breaking down of polluting aromatic compounds in petrochemical plants:



(I)

in which X= H, NH_2

n= 0 or positive integer number
R_1, R_2, being equal or different from each other, are H, linear, branched or cyclic aliphatic chain C_1-C_{10}, or R_1 and R_2 are joined together to form an aromatic cycle, substituted with the $(SO_2X)_n$ group if necessary taking care that at least one $(SO_2X)_n$ group is always present in the molecule; the corresponding salts of the formula (I) compounds and the corresponding mixtures.

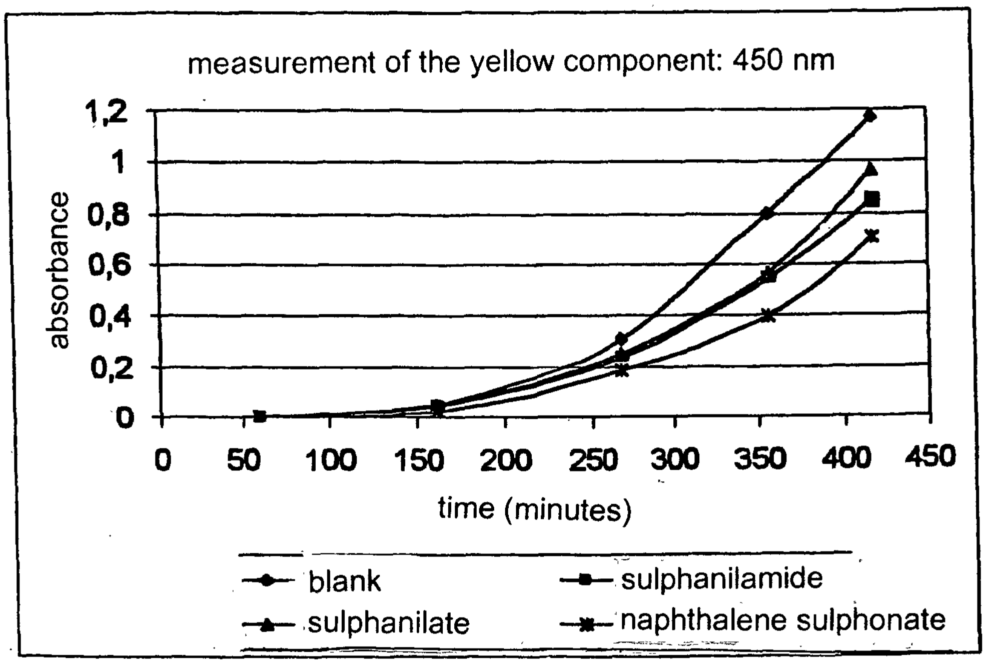

measurement of the yellow component: 450 nm
absorbance
1,2
1
0,8
0,6
0,4
0,2
0
0
50
100
150
200
250
300
350
400
450
time (minutes)
blank
sulphanilamide
sulphanilate
naphthalene sulphonate

Fig. 1

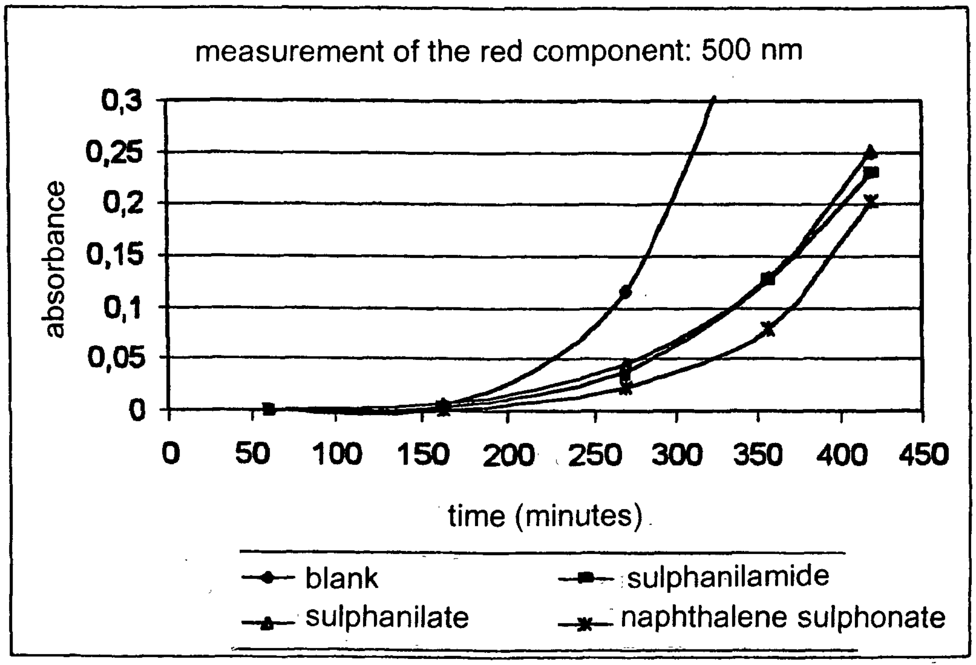

measurement of the red component: 500 nm
absorbance
0,3
0,25
0,2
0,15
0,1
0,05
0
0
50
100
150
200
250
300
350
400
450
time (minutes)
blank
sulphanilamide
sulphanilate
naphthalene sulphonate

Fig. 2

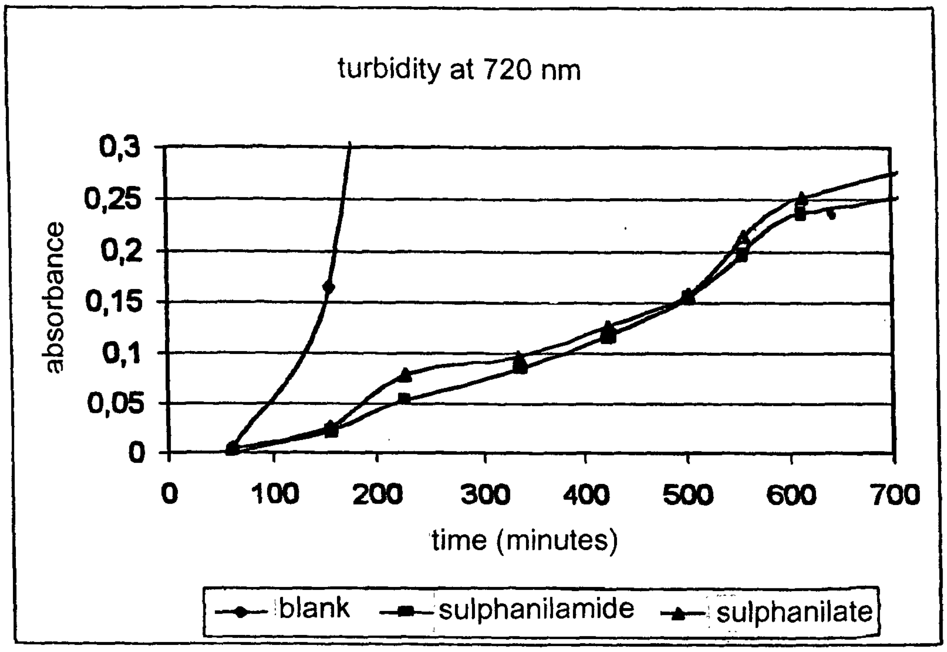
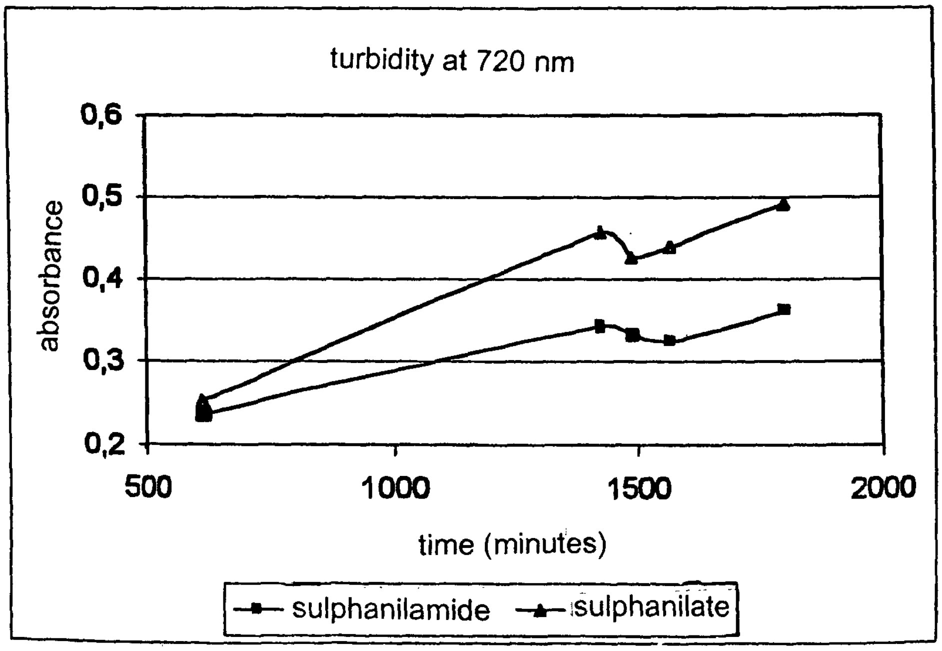

turbidity at 720 nm
absorbance
0,3
0,25
0,2
0,15
0,1
0,05
0
0
100
200
300
400
500
600
700
time (minutes)
blank
sulphanilamide
sulphanilate

Fig. 3


turbidity at 720 nm
absorbance
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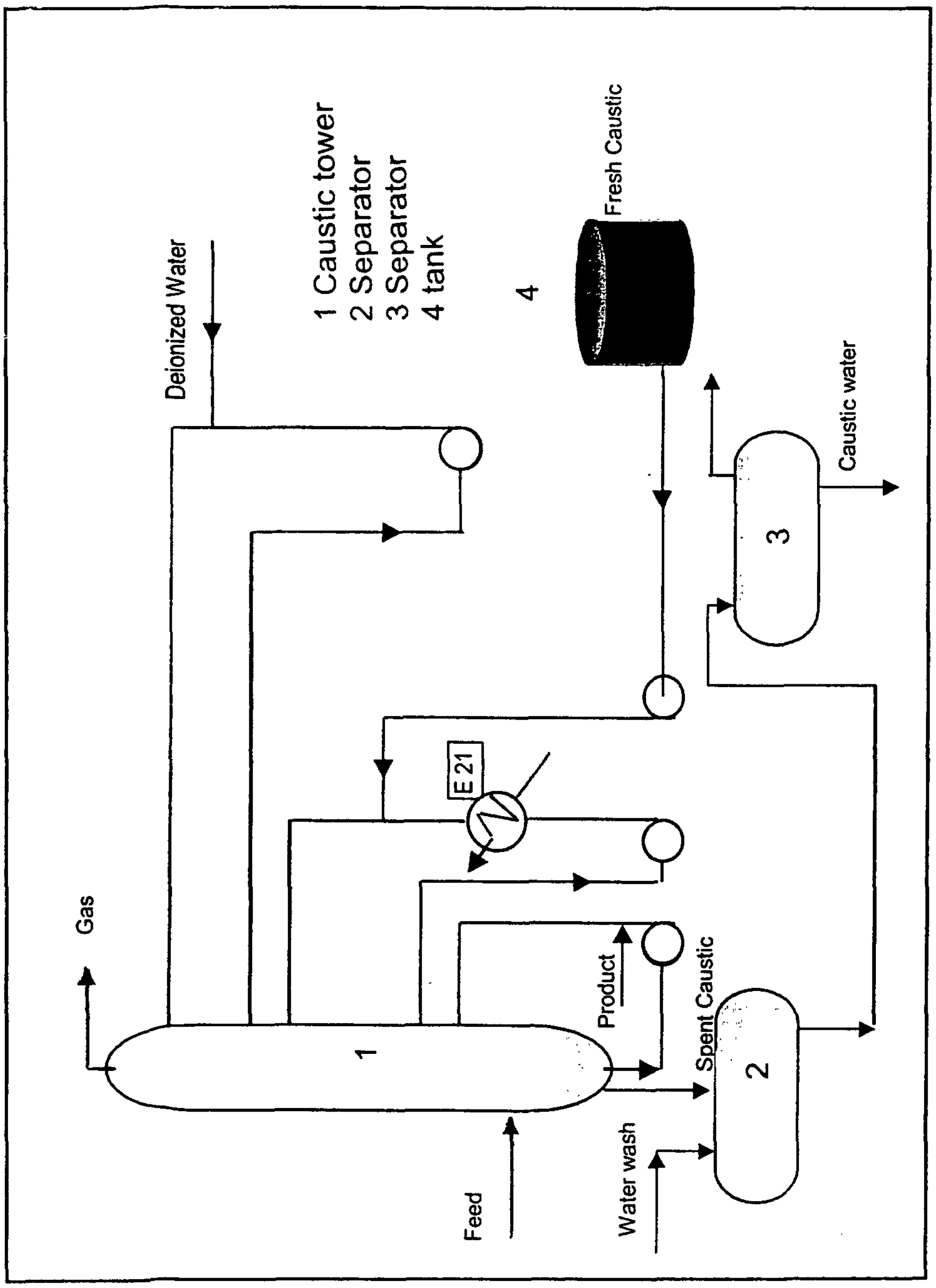
0,3
0,2
500
1000
1500
2000
time (minutes)
sulphanilamide
sulphanilate

Fig. 4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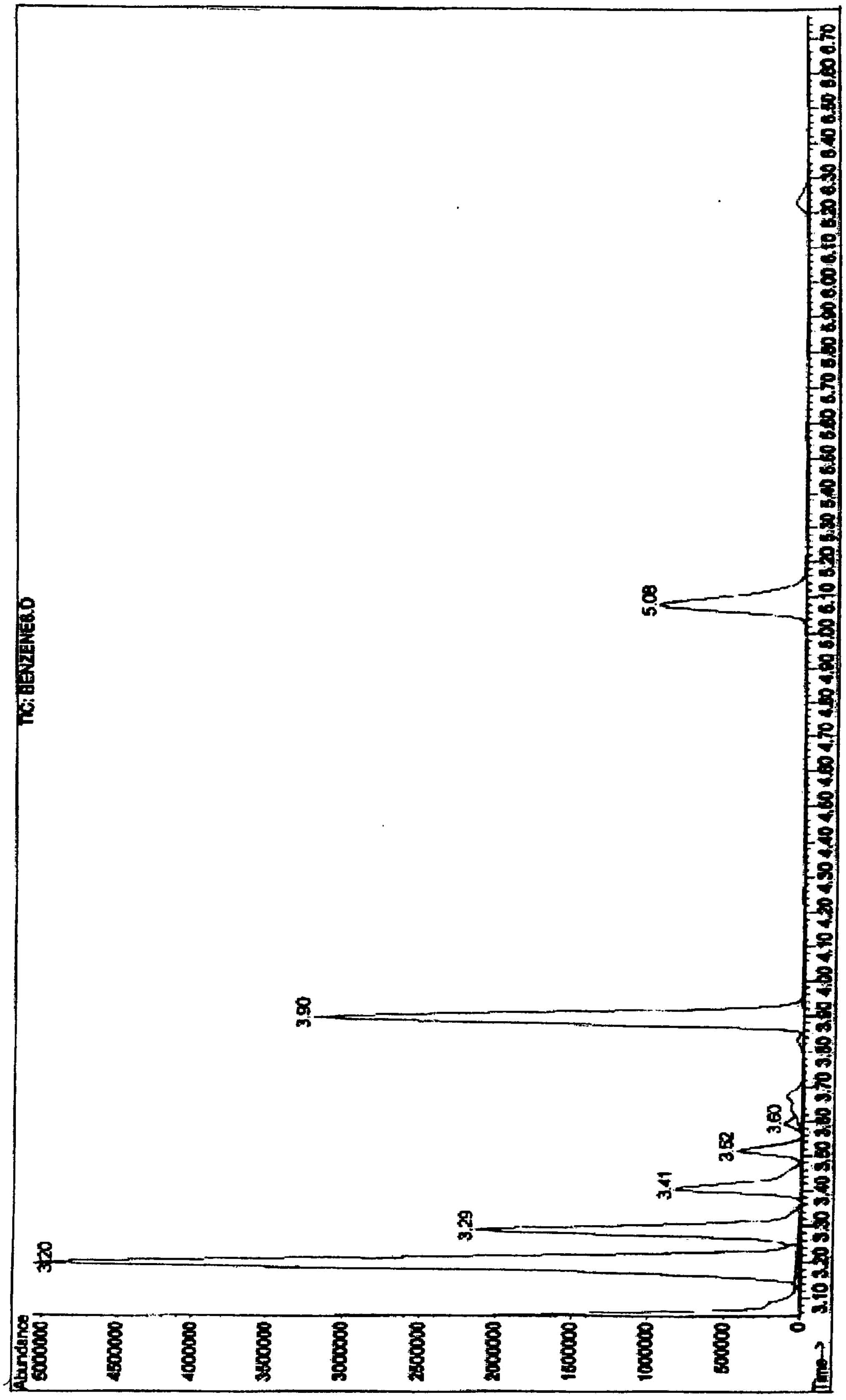
1 Caustic tower
2 Separator
3 Separator
4 tank
4
Fresh Caustic
Caustic water
3
E 21
Gas
Product
Spent Caustic
1
2
Feed
Water wash

FIGURE 5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4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
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3.20
3.29
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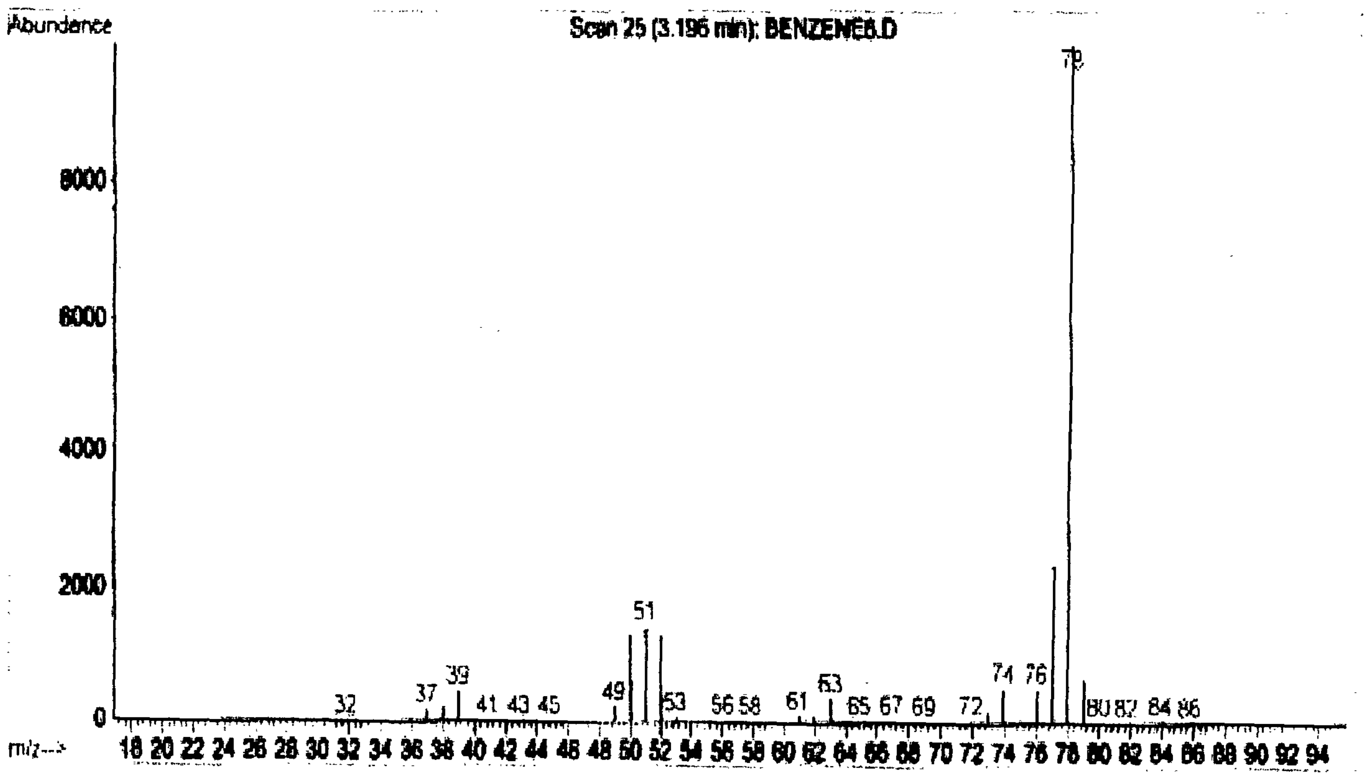
3.52
3.60
3.90
5.08

FIGURE 6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6000
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m/z-->
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32
37
39
41
43
45
49
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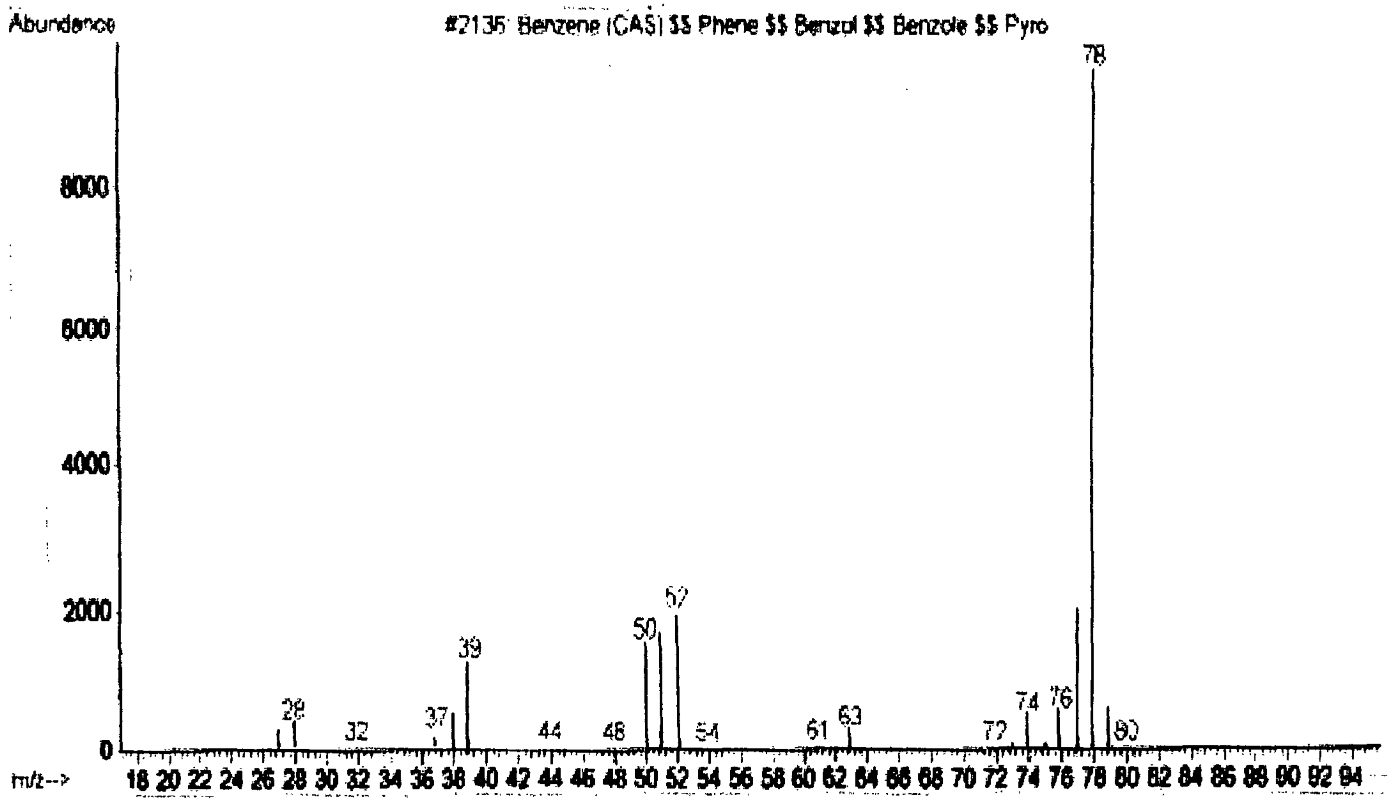
74
76
78
80
82
84
86

FIGURE 7a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6000
4000
2000
0
m/z-->
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FIGURE 7b

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 12 8550

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Place of search	Date of completion of the search	Examiner
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