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(54) **FUEL OIL ADDITIVE**

HEIZÖLADDITIV

ADDITIF POUR MAZOUT

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(73) Proprietor: **CHIMEC S.P.A.**
I-00144 Roma RM (IT)

(72) Inventors:
• **ZANOTTI, Andrea**
I-00042 Anzio (IT)
• **BUCCOLINI, Marco**
I-62032 Camerino (IT)

• **MANTARRO, Milena**
I-00177 Roma (IT)

(74) Representative: **Gervasi, Gemma**
Studio Brevetti e Marchi
NOTARBARTOLO & GERVASI S.r.l.,
Corso di Porta Vittoria, 9
20122 Milano (IT)

(56) References cited:
EP-A- 0 580 308 GB-A- 1 054 140
GB-A- 1 078 772 US-A- 3 849 370
US-A- 4 321 218 US-A- 5 726 131

• **PATENT ABSTRACTS OF JAPAN vol. 0031, no.**
30 (M-078), 27 October 1979 (1979-10-27) & JP 54
105648 A (NIPPON OIL & FATS CO LTD), 18
August 1979 (1979-08-18)

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DescriptionField of the invention

[0001] The present invention relates to an additive for fuel oil, in particular fuel oil leaving Visbreaking (VSB) plants.

Known art

[0002] Visbreaking (VSB) is a thermal conversion process applied to petroleum distillation residues, otherwise intended for bitumen or fuel oil (products which are well-known to be of low commercial value), to partially convert them into lighter products of higher value. The conversion provides in part distillation products such as gas, petrols, kerosene, gas oil and in part residue (hereinafter also referred to as tar or TAR), that can still constitute the basis for use as fuel oil. The conversion process is conducted in such a manner as to maximise the yield of distillation products, while reducing the overall yield of tar oil. It should be noted that even a conversion increase equal to 1% of the feedstock is be considered extremely satisfactory in terms of economic yield.

[0003] The VSB plant, as illustrated schematically in Figure 1 attached, comprises the following parts: a heat exchanger bank (A) through which the feedstock enters the VSB plant for pre-heating; a furnace (B) in which the actual thermal cracking takes place; and a fractionation column (C), from the top of which the distillates are extracted and from the bottom of which the residue (TAR) leaves. This residue passes through a heat exchanger bank (D) to transfer part of its heat to the feedstock and is then stored in tanks (E). A soaker and a preflash column (not shown) can be provided between the furnace and the fractionation column.

[0004] The VSB plant operative conditions, known to the expert of the art, may be briefly described as follows: a feedstock, consisting generally of a primary or vacuum distillation residue, is fed into the furnace (B) which operates at temperatures ranging from 420°C to 500°C and at pressures of between 3 bar and 20 bar. The feedstock treated in this manner passes to the fractionating column (C), which operates using known procedures, for example as described in patent application EP0818524; from it the following products can be obtained, for example in the following proportions: light distillates (gas and petrols, 3-10%), medium distillates (kerosene and gas oil, 15-20%) and a residue (TAR, 65-75%); the percentages are by weight on the total products leaving the VSB plant.

[0005] The TAR, present in a greater proportion than the other components, must conform to specifications set by the market, for example those indicated in Table 1, if it is to be used as fuel oil.

TABLE 1

Determination		Method	Specification
Water and sediments	%v	ASTM D 1796	Max 0.5
Asphaltenes	%w	IP 143***	Max 6
Heat of combustion	Kcal/Kg	ASTM D 240	Min 9.850
Ash	%w	ASTM D 482	Max 0.03
Density at 15°C	Kg/m ³	ASTM D 1298	Max 990
Distillation at 300°C	%v	ASTM D 86	Max 60*
Distillation at 350°C	%v	ASTM D 86	< 85*
HFT (Hot Filtration Test)	%w	ASTM D 4870	Max 0.20
Inflammability, Pensky Martens	°C	ASTM D 93	Min 65
Upper pour point	°C	ASTM D 97	Max +40
Conradson carbon residue	%w	ASTM D 189	Max 13
Nickel	ppm	SAA****	Max 60
Sodium	ppm	SAA****	Max 100
Vanadium	ppm	SAA****	Max 90
Viscosity at 50°C	cst	ASTM D 445	Max 400*
Viscosity at 50°C	°E**	ASTM D 455	Max 52.6*

Table continued

Determination	Method	Specification
Sulphur %w	ISO14596	Max 1.0*
*required by Italian law ** viscosity °E at 50°C greater than 12 and ASTM colour diluted min 4.0 ***IP: The Institute of Petroleum (recognised standard method); ****SAA: Spectrophotometry by Atomic Absorption		

[0006] Usually the plant is operated so that the TAR obtained, except for slight viscosity corrections, already satisfies the required specifications for fuel oil, and as such "TAR" and "fuel oil" shall be hereinafter considered synonyms for the purposes of the present invention.

[0007] Patent application EP0818524 describes a method for decreasing the viscosity of the TAR, for equal distillates leaving the plant, but the tar thus produced has the drawback of being unstable with time.

[0008] The fuel oil leaving the plants is stored in tanks where it is maintained at a temperature between 70°C and 110°C until the time of its pumping into tankers or its arrival in the burners. This time can be some weeks.

[0009] During these manipulations, the oil comes into contact with air and is subjected to heat, which, combined with the variable time, can facilitate the formation of insoluble compounds in the oil.

[0010] In this respect it has been noted that, over time, i.e. during storage in the tanks, the fuel oil shows ageing phenomena, indicated by a progressive increase in the HFT value (indicating the presence of sediments) until the fuel oil, even within a very short time, of the order of a few days, lies outside specification.

[0011] The aged TAR no longer conforms to specifications required by the market; its viscosity increases so as has its HFT value. This results operationally in TAR pumpability difficulties and above all, on use (combustion), the occurrence of the following drawbacks:

- Abundant formation of carbon in the preheaters, due to the coking of heavy carbon containing materials
- Abundant formation of soot produced by the incomplete combustion of precipitated insoluble heavy compounds
- Sediments, paraffins and substances similar to gum occurring in the lines of the combustion system

[0012] Current solutions adopted to counteract the instability of TAR all have drawbacks. For example, the exit temperature of the VSB plant furnace (B) can be lowered, but this reduces the production of (valuable) light products. Alternatively the TAR can be mixed with suitable distillates, for example gas oil, to counteract the separation of the insoluble compounds present in the oil, but in this manner a low value-added product is diluted with other products of a higher added value. In both cases, therefore, the solutions adopted have too high a cost. The problem of effective and at the same time economically advantageous stabilisation of TAR or fuel oil consequently remains unsolved to this day.

[0013] An additive has now been found to counteract the increase of HFT in fuel oil during storage; this additive solves the aforesaid problems.

Field of the invention

[0014] The present invention refers to a composition to be added to fuel oil to render it storage stable and to counteract the formation of insolubles. More particularly the composition according to the invention comprises the mixture of the following classes of products: at least one compound pertaining to the organic phosphite class in which the patom is bonded to at least one aromatic ring, at least one compound pertaining to the sterically hindered phenol class, at least one compound pertaining to the formate class.

[0015] Another object of the invention is the method for stabilising fuel oil, characterised by adding the additive according to the invention to the TAR leaving the VSB column in the line leading to the storage tank (E).

[0016] Further objects will become evident from the detailed description of the invention.

Brief description of the figures

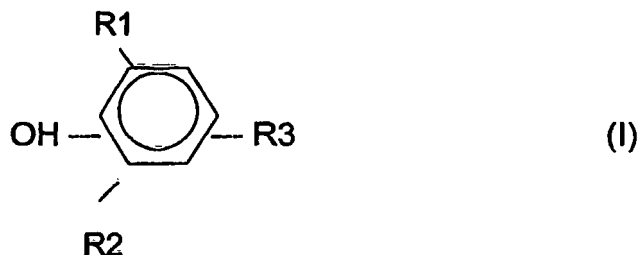
[0017]

Figure 1 illustrates schematically a VSB plant.

Detailed description of the invention

[0018] The composition of the additive according to the invention is a mixture of at least two active principles, each in proportion from 5% to 95% by weight on the total composition, chosen from the following group:

- (a) At least one organic phosphite;
- (b) At least one hindered phenol of general formula (I):



in which: R1=t-butyl group; R2=linear or branched C1-C5 carbon atom chain; R3=H, linear or branched C1-C5 carbon atom chain. Preferred are compounds with: R2=C(CH₃)₃ and R3=H or R2=C(CH₃)₃ and R3=CH₃.

- (c) At least one formate, in particular trimethyl-orthoformate;

said composition being characterised by being soluble in fuel oil, preferably at a temperature between 50° and 300°C.

[0019] Organic phosphites are a class of compounds well known to the expert of the art and are for example described in "Nuovo dizionario di merceologia e chimica applicata", Villavecchia Eigenmann, Vol. 4 Fisostigmina-Mangimi, page 1558, or in patents U.S. 6,362,260B1; EP 1028142A2; U.S. 5,614,571; U.S. 4,321,218; U.S. 3,897,388; W.O. 96/17913; U.S. 3,969,315, which describe the application of phosphites as stabilisers for various uses. Preferred are phosphites in which the P atom is bonded to at least one aromatic ring, possibly alkyl-substituted. Particularly preferred are triphenylphosphite (TPP) and methyl-di-phenylphosphite, possibly in which at least one phenyl group is substituted by an alkyl radical (nonyl).

[0020] The formates are a class of compounds well known to the expert of the art and are for example described in U.S. 4,347,175. Preferred are the alkyl formates. Particularly preferred is trimethyl-ortho-formate (TMOF).

[0021] Any proportions (% by weight) of the active ingredients indicated above can be used; preferred are ternary mixtures with the following ratios: (a):(b):(c), with (a) variable from 1 to 5, (b) variable from 1 to 3 and (c) variable from 1 to 3; particularly preferred is the following percentage composition: 47.6% of (a), in particular triphenylphosphite (TPP), 23.8% of (b), in particular di-tert-butyl-hydroxytoluene (BHT) and 28.6% of (c), in particular trimethyl-orthoformate (TMOF) (ratio 2:1:1.7)

[0022] A method for stabilising TAR according to the present invention is one which provides a stage of adding the composition according to the invention directly to the line that connects the bottom of the fractionation column (C) to the TAR storage tank (E).

[0023] The preferred quantities are between 50 and 200 ppm on the fuel oil or tar.

[0024] The most obvious advantage of the invention is that the commercial specifications required by the market for oil thus treated are guaranteed at very low additional costs.

[0025] The following examples are given to illustrate the invention and are not to be considered as limiting the scope thereof.

ExamplesPreparation of the blank sample and additive-treated sample.

[0026] A portion of fuel oil is heated for about 20 minutes in an oven at 110°C. A known volume of the sample (100g) is taken. The sample is placed on a plate at 105°C and the compositions indicated below are added, taking great care to fully mix them into the sample using a magnetic agitator or glass rod, with agitation on the plate for 15 minutes. The samples, with or without additive, are then placed in the oven or in a temperature controlled bath for 24 hours at 100°C to simulate ageing.

[0027] The blank sample contained no additive. The compounds used in the additive treatment were the following:

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(a) TPP supplied by Atofina Italia, (b) BHT supplied by Pantrade, (c) TMOF supplied by Romana Chimici.

Binary compositions (% by weight): (a) 66.7; (b) 33.3

Ternary compositions (% by weight): (a) 47.6; (b) 23.8; (c) 28.6

[0028] The TAR (VSB residue) used in the tests had the specifications reported in Tab. 2.

Table 2

Determination	Method	Specification
Density at 15°C Kg/m ³	ASTM D 1298	0.953
%S %w	IS014596	0.81
Viscosity at 50°C cst	ASTM D 445	35.5
PV	Shell Method	1.1
HFT %w	ASTM D 4870	<0.01

[0029] This matrix was processed according to ASTM D 4870, following ageing in the oven at 100°C for 24 hours, to determine the total sediments content and this value was compared with that obtained on the same sample with the mixtures of the invention added.

Determination of sediment contents

[0030] After 24 hours the samples are removed from the oven or from the temperature controlled bath and the HFT value is determined according to the ASTM D 4870 method.

[0031] Tests were carried out with the compounds indicated above containing a single additive (Table 3), or in binary mixture (Table 4) or in ternary mixture (Table 5).

[0032] The amount of additive added, consisting of the products listed in the aforesaid tables in the percentages indicated, was in each test equal to 200 ppm.

[0033] In the tables the $\Delta\text{HFT}\%$ value is calculated as indicated below:

$$\Delta\text{HFT}\% = 100 * (\text{HFT}_{\text{blank}} - \text{HFT}_{\text{additive-treated}}) / (\text{HFT}_{\text{blank}})$$

where:

$\text{HFT}_{\text{blank}}$ is the value of HFT in the untreated sample

$\text{HFT}_{\text{additive-treated}}$ is the value of HFT in the sample treated with the additive of the invention.

Table 3

Product	HFT (%w/w)	$\Delta\text{HFT}\%$
Blank	0.43	
TPP 100%	0.32	26.5%
BHT 100%	0.34	21.3%

Table 4

Product	HFT (%w/w)	$\Delta\text{HFT}\%$
Blank	0.43	
TPP (66.7) - BHT (33.3)	0.24	44.2

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Table 5

Product	HFT (%w/w)	Δ HFT%
Blank	0.43	
MixE=TPP(47,6)-BHT(23,8)-TMOF(28,6)	0.18	58.1%

[0034] By comparing the data in the tables, it can be deduced that the best result compared with blank sample was obtained with the ternary mixture, namely Mix E, with an efficiency greater than 50%.

Plant test

[0035] The mixture Mix E was also tested in a VSB plant during a six day industrial trial.

[0036] In order to adequately illustrate the trial it is important to recall the following concept, namely that the VSB plant is operated with the aim of obtaining maximum conversion into medium and light distillates (high value added products). This aim is achieved by increasing the furnace exit temperature (FET), but this has the disadvantage of obtaining an unstable tar which falls easily outside specification.

[0037] The composition of the invention allows the FET to be raised while at the same time obtaining a stable Tar.

[0038] The mixture Mix E was additive-treated with an average amount of approximately 100 ppm on a TAR, whose characteristics correspond to those in table 2. The samples poured from the heat exchanger bank (D), were subjected to analysis prior to ageing in an oven for 24 hours and the results are reported in table 6.

HFT_{24h} additive-treated (%w/w): value of sediment content in the sample withdrawn after the treatment with additive

HFT_{24h} blank (%w,w): value of sediment content in the sample withdrawn before the treatment with additive

Table 6

Sample	HFT _{24h} additive-treated (%w/w)	HFT _{24h} blank (%w/w)	Δ HFT%
Mix E:100 ppm - FET +3°C	0.02	0.04	50.0
Mix E: 50 ppm - FET +3°C	0.04	0.08	50.0
Mix E: 50 ppm - FET +3°C	0.07	0.10	30.0
Mix E:100 ppm - FET +5°C	0.08	0.15	46.7
Mix E: 150 ppm - FET +5°C	0.18	0.25	28.0
Mix E:150 ppm - FET +5°C	0.18	0.26	30.8
Tank	0.197		

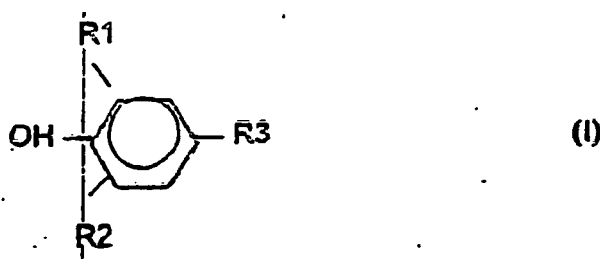
[0039] As shown in the data reported in table 6, the product Mix E used in the plant demonstrates an average efficiency in the order of 40%. As the table data show, increasing the FET by a minimum of +3°C to a maximum of +5°C (FET_{initial}=487°C) and therefore the severity of the system, the HFT values calculated on the samples with the stabiliser added demonstrate a valuable containment of ageing. This phenomenon, quantifiable as Δ HFT%, lies within the range 28-50%.

[0040] The additive-treated TAR was collected during the time taken for the trial, in a storage tank (E) and at the end of this time, a representative sample, withdrawn from the tank, was subjected to HFT analysis showing a value which conforms to the required commercial specifications, In accordance with the tables.

Claims

1. Stabilising composition for fuel oil or tar able to counteract the formation of solids contained therein, said composition comprising the mixture of the following classes of products: at least one compound pertaining to the organic phosphite class (a) in which the P atom is bonded to at least 1 aromatic ring, at least one compound pertaining to the sterically hindered phenol class (b), at least one compound pertaining to the formate class (c), each in a proportion from 5% to 95% by weight on the total composition.
2. Composition according to claim 1, added to the tar in amounts ranging between 50 and 200 ppm.

3. Composition according to claim 1, wherein the hindered phenol has the general formula (I):

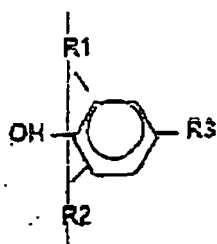


in which R1=t-butyl group; R2=linear or branched C1-C5 carbon atom chain; R3=H, linear or benched C1-C5 carbon atom chain.

- 15
4. Composition as claimed in claim 3 wherein R2=C(CH₃)₃ and R3=H or R2:C(CH₃)₃ and R3=CH₃
5. Composition according to claim 1 wherein the formate is trimethyl-orthoformate.
- 20
6. Composition as claimed in claim wherein the phosphite P atom is bonded to at least 1 aromatic ring, possibly alkyl-substituted.
7. Composition according to claim 6, wherein the phosphite is chosen from: triphenylphosphite (TPP) and methyl-di-phenylphosphite, possibly in which at least a phenyl group is substituted with an alkyl radical.
- 25
8. Composition according to claim 1, **characterised in that** it is soluble in fuel oil at a temperature between 50° and 300°C.
9. Composition according to claim 1, wherein the additive components are in the following ratios (a):(b):(c), with (a) variable from 1 to 5, (b) variable from 1 to 3 and (c) variable from 1 to 3.
- 30
10. Composition according to claim 1 comprising: 47.6% by weight of (a), 23.8% by weight of (b) and 26.6% by weight of (c).
- 35
11. Composition according to claim 10, wherein (a) is triphenylphosphite, (b) is ditert-butyl-hydroxytoluene and (c) is trimethyl-orthoformate.
12. Fuel oil or tar comprising a composition according to any of claims 1-11.
- 40
13. Method for stabilising tar or fuel oil deriving from the VSB process, **characterised in that** an additive according to claims 1-11 is added to the TAR leaving the VSB column (C) in the line connecting the bottom of (C) to the TAR storage tank (E).

45 **Revendications**

1. Composition stabilisante pour du mazout ou pour du goudron capable de contrecarrer la formation des solides qui y sont contenus, ladite composition comprenant le mélange des classes suivantes de produits : au moins un composé appartenant à la classe des phosphites organiques (a) dans lequel l'atome P est lié à au moins 1 cycle aromatique,
- 50
- au moins un composé appartenant à la classe du phénol encombré stériquement (b), au moins un composé appartenant à la classe du formate (c), chacun dans une proportion de 5 % à 95 % en poids de la composition totale.
2. Composition selon la revendication 1, ajoutée au goudron en quantités comprises entre 50 et 200 ppm.
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3. Composition selon la revendication 1, dans laquelle le phénol encombré a la formule générale (I) :



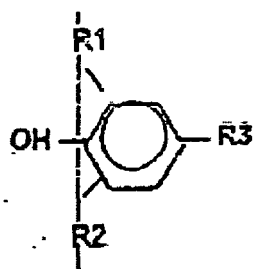
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dans laquelle R1 = groupe t-butyle ; R2 = chaîne linéaire ou ramifiée d'atomes de carbone en C1 à C5 ; R3 = H, chaîne linéaire ou ramifiée d'atomes de carbone en C1 à C5.

4. Composition selon la revendication 3, dans laquelle R2 = C(CH₃)₃ et R3 = H ou R2 = C(CH₃)₃ et R3 = CH₃.
5. Composition selon la revendication 1, dans laquelle le formate est de l'orthoformate de triméthyle.
6. Composition selon la revendication 1, dans laquelle l'atome de phosphite P est lié à au moins un cycle aromatique, éventuellement substitué par un alkyle.
7. Composition selon la revendication 6, dans laquelle le phosphite est choisi parmi : le triphénylphosphite (TPP) et le méthyl-di-phénylphosphite, éventuellement dans lesquels au moins un groupe phényle est substitué avec un radical alkyle.
8. Composition selon la revendication 1, **caractérisée en ce qu'elle** est soluble dans le mazout à une température entre 50°C et 300°C.
9. Composition selon la revendication 1, dans laquelle les composants de l'additif sont dans les rapports suivants (a) / (b) / (c), (a) étant variable de 1 à 5, (b) étant variable de 1 à 3 et (c) étant variable de 1 à 3.
10. Composition selon la revendication 1, comprenant : 47,6 % en poids de (a), 23,8 % en poids de (b) et 28,6 % en poids de (c).
11. Composition selon la revendication 10, dans laquelle (a) est du triphénylphosphite, (b) est du ditert-butyl-hydroxy-toluène et (c) est de l'orthoformate de triméthyle.
12. Mazout ou goudron comprenant une composition selon l'une quelconque des revendications 1 à 11.
13. Procédé pour stabiliser du goudron ou du mazout dérivé à partir du procédé VSB, **caractérisé en ce qu'un** additif selon les revendications 1 à 11 est ajouté au goudron quittant la colonne VSB (C) dans la ligne connectant le fond de (C) au réservoir de stockage de goudron (E).

Patentansprüche

1. Stabilisierende Zusammensetzung für Heizöl oder Teer, welche der Bildung von darin enthaltenen Feststoffen entgegenwirken kann, wobei genannte Zusammensetzung die Mischung der folgenden Klassen von Produkten umfasst: mindestens eine Verbindung, welche die Klasse der organischen Phosphite (a) betrifft, in welcher das P-Atom an mindestens 1 aromatischen Ring gebunden ist, mindestens eine Verbindung, welche die Klasse der sterisch gehinderten Phenole (b) betrifft, mindestens eine Verbindung, welche die Klasse der Formiate (c) betrifft, jedes in einem Anteil zwischen 5 Gew.-% bis 95 Gew.-% der gesamten Zusammensetzung.
2. Zusammensetzung gemäß Anspruch 1, welche zu dem Teer in Mengen zwischen 50 und 200 ppm gegeben wird.
3. Zusammensetzung gemäß Anspruch 1, in welcher das gehinderte Phenol die allgemeine Formel (1) aufweist:



in welcher R1 = tert.-Butylgruppe, R2 = lineare oder verzweigte C₁-C₅-Kohlenstoffatomkette, R3 = H, lineare oder verzweigte C₁-C₅-Kohlenstoffatomkette

4. Zusammensetzung gemäß Anspruch 2, in welcher R2 = C(CH₃)₃ und R3 = H oder R2 = C(CH₃)₃ und R3 = CH₃.
5. Zusammensetzung gemäß Anspruch 1, in welcher das Formiat Orthoameisensäuretrimethylester ist.
6. Zusammensetzung gemäß Anspruch 1, in welcher das Phosphit-P-Atom an mindestens 1 aromatischen Ring gebunden ist, der gegebenenfalls Alkyl-substituiert ist.
7. Zusammensetzung gemäß Anspruch 6, in welcher das Phosphit ausgewählt wird aus: Triphenylphosphit (TPP) und Methyl-di-phenylphosphit, in welchen gegebenenfalls mindestens eine Phenylgruppe mit einem Alkylrest substituiert ist.
8. Zusammensetzung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** sie in Heizöl bei einer Temperatur zwischen 50° und 300°C löslich ist.
9. Zusammensetzung gemäß Anspruch 1, in welcher die Additivbestandteile in den folgenden Verhältnissen vorliegen (a):(b):(c), mit (a) zwischen 1 bis 5, (b) zwischen 1 bis 3 und (c) zwischen 1 bis 3 variierend.
10. Zusammensetzung gemäß Anspruch 1, umfassend: 47,6Gew.-% (a), 23,8 Gew.-% (b) und 28,6 Gew.-% (c).
11. Zusammensetzung gemäß Anspruch 10, in welcher (a) Triphenylphosphit, (b) Di-tert-butylhydroxytoluol und (c) Orthoameisensäuretrimethylester ist.
12. Heizöl oder Teer, umfassend eine Zusammensetzung gemäß einem der Ansprüche 1 - 11.
13. Verfahren zur Stabilisierung von Teer oder Heizöl, ausgehend vom VSB-Verfahren, **dadurch gekennzeichnet, dass** das Additiv gemäß einem der Ansprüche 1-11 zu dem Teer gegeben wird, welcher die VSB-Säule (C) über die Leitung verlässt, welche den Boden von (C) mit dem Teerlagertank (E) verbindet.

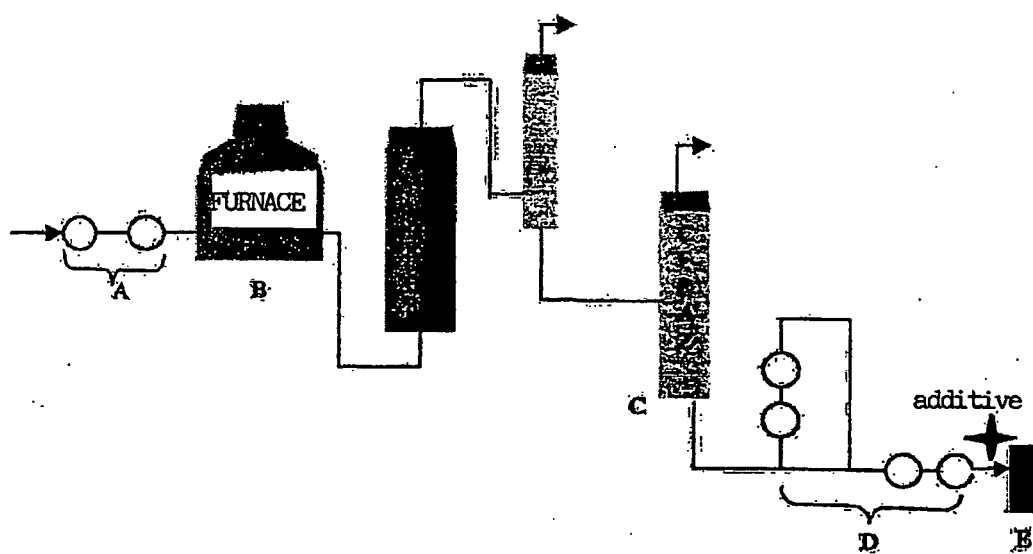


Fig.1