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(54) GASOLINE STABILIZING COMPOSITION FOR PREVENTING GUM FORMATION

BENZIN STABILISIERENDE ZUSAMMENSETZUNG ZUR GUMMIBILDUNGVERHINDERUNG

COMPOSITION DE STABILISATION A BASE D'ESSENCE POUR PREVENIR LA FORMATION DE GOMME

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Description

Background of the Invention

[0001] The present invention relates to the stabilization of gasoline for preventing gum formation, specifically it relates to gasolines obtained by steam cracking. However, the stabilizing composition according to the invention is also effective in the stabilization of gasolines outputted from thermal (e.g., Visbreaking, coking and the like), or catalytic (e.g. Fluidized Catalytic Cracking) cracking plants.

[0002] The stabilization according to the invention is obtained by use of a composition comprising phenothiazine (PNTZ) and tert.butyl catechol, unexpectedly providing, at certain use ratios, a synergistic stabilizing effect.

[0003] The term «gasolines» refers to the fuels for the normal internal combustion engines, made of blends of hydrocarbons that may widely differ one from the other according to the production process thereof.

Background of the prior art

[0004] As it is well-known, all gasolines are subject, especially upon storage, to degradation phenomena leading to the formation of gum-like polymeric substances, producing sticky deposits. These substances are known to cause severe clogging and sticking problems to the filters, the valves and the transfer pumps, besides adversely effecting the combustion performance of the gasoline itself.

[0005] Among the various gasolines, the stability issue is particularly critical for those gasolines outputted from cracking plants, containing, in fact, a relatively high amount of hydrocarbons having double bonds readily polymerizable in presence of free radicals (unsaturated hydrocarbons).

[0006] The stability problem is particularly critical for gasolines produced by a steam cracking process. However, the problem concerns any thermal (visbreaking, coking, thermal cracking), as well as catalytic (FCC, LC finer, Mild Hydrocracking, HDS) cracked gasoline.

[0007] In the present context, the stability is evaluated as resistance to degradation caused by oxygen contact.

[0008] In the prior art, in order to eliminate or reduce the incidence of the above-mentioned problems, stabilizers added to the gasoline for enhancing the stability thereof were used.

[0009] Effective stabilizers for gasolines of the prior art belong to the class of the aromatic amines. For instance, paraphenylenediamines (PDA), that can also be used in admixture with other materials, like, e.g., the nitroxides (US-A-5,711,767) or the hindered phenols (US-A-5,509,944).

[0010] Other examples thereof are the N-substituted p-aminophenols (US-A-2,305,676 and 2,333,204), the polyamines and the hydroxylamines (US-A-4,648,885).

[0011] Even though their effectiveness is indisputable, their use is clearly unadvisable due to the hazardousness thereof, as highlighted by the actual toxicological knowledge.

[0012] In fact, due to their carcinogenicity confirmed by testing on animals and corroboration on human beings, several substances belonging to this class have been disallowed, as reported by various International organizations (EPA, CEE and others), that tend to consider every aromatic amine as a potential carcinogen.

[0013] The use of phenotiazine, alone or in admixture with other materials, is known to stabilize monomers and as an antifouling agent in oil or petrochemical processes, and overall as a polymerization inhibitor of vinyl aromatic compounds (US-A-4,061,545).

[0014] The use as stabilizers of spontaneously polymerizing monomers of phenols, and in particular of TBC, has been long-time known, for various monomers marketed as reactants or for industrial use (styrene, butadiene and the like).

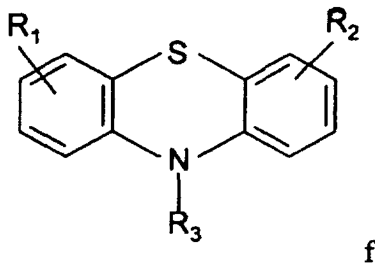
[0015] Moreover, the TBC is used in many stabilizing-antifouling agent combinations when an inhibition of polymerization reactions is required, (US-A-3 553 990), and as a retarding agent in the formation of coke and of fouling in petrochemical processes.

Description of the Invention

[0016] Therefore, it is an object of the present invention the use of a gasoline stabilizing composition, for inhibiting a gasoline degradation by preventing gum formation in said gasoline,

wherein said stabilizing composition comprises as effective inhibition ingredients:

A) substituted or unsubstituted phenothiazine (PNTZ) of formula

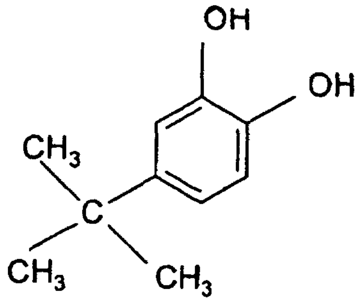


formula (1)

wherein R_1 and R_2 represent H, an alkyl C_1 - C_{20} or a cycloalkyl C_5 - C_{20} group and R_3 represents H, an alkyl C_1 - C_{20} or cycloalkil C_5 - C_{20} and phenyl group, said alkyl and cycloalkyl groups possibly also containing functional groups,

or dimer phenothiazine; and

B) 4-tert.butyl-catechol (TBC) of formula

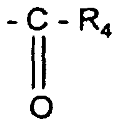


formula (2)

in a ratio of 5:95 to 80:20 therebetween.

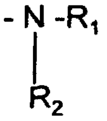
[0017] As functional groups possibly contained in the substituted PNTZ of formula (1), there could be, e.g.:

esther or carboxylic acid groups and derivatives thereof, of the type



$$-\underset{\underset{O}{\|}}{C}-R_4$$

wherein R_4 is H, OH, R_3, $-OR_1$, or $-OR_3$;
alcohol or esther groups of the $-O-R_3$ type;
amino groups of the type



$$-\underset{\underset{R_2}{|}}{N}-R_1$$

or mercaptane or sulfur groups of the $-S-R_1$ type.

[0018] A novel solution to the problem of gasolines stabilization and prevention of gum formation is provided by the use of a composition of PNTZ and of TBC in a suitably balanced ratio therebetween, having low toxicity and high effectiveness, equal to or higher than that of the PDA, and void of carcinogenic hazards, in the stabilization of pyrolisis gasolines, particularly of catalytic cracking gasolines.

[0019] Therefore, the subject-matter of the present invention is the use of a gasoline stabilizing composition for preventing the gum formation and the degradation thereof, characterized in that it comprises, as effective preventing components, substituted or unsubstituted phenothiazine (PNTZ) or dimer, and tert.butyl-catechol (TBC) in a certain ratio therebetween, as well as the use thereof as a stabilizer, the gasolines thus stabilized and the related gasoline stabilization method.

[0020] According to the present invention, the gasoline stabilization is carried out by adding to the gasoline 5 to 1000 ppm of a stabilizer, comprising as active stabilizing ingredients PNTZ and TBC in a weight ratio therebetween of 5:95 to 80:20, preferably of 27:75 to 40:60, even more preferably of 30:70 to 35:65, with an optimum value of about 33.3:66.6.

[0021] The dosage of the additive with respect to the gasoline, as well as the ratio of the two compounds, can vary with particular reference to the Bromine number and to the diene value.

[0022] The composition according to the invention may contain, besides the two above-mentioned components, PTNZ and TBC, other PTNZ- and TBC- compatible components and additive carriers commonly used in stabilizing compositions. Particularly suitable solvents are the aromatic solvents, like benzene, toluol and the like, as well as dimethyl-formamide and dimethyl-acetamide.

[0023] The combined use of the compounds in the blend yields a synergistic effect that is particularly significant at the preferred weight ratio values of the compounds.

EMBODIMENTS

[0024] The effectiveness of the stabilizing blend according to the invention was measured in tests that will hereinafter be disclosed.

[0025] Stability measurement tests use an assay for measuring the stability to degradation of the gasolines denominated Induction Period (Time?) Method ASTM D525. This method is deemed the most suitable for measuring the stability of the gasolines, by virtue of the predictive capacity thereof of the gum formation due to a gasoline polymerization in presence of oxygen.

[0026] Such method provides the heating at 100°C (98°C-102°C) of a 50 ml sample in a bomb, sealed and subjected to a 690 kPa (100 psi) air pressure.

[0027] The test attains a break point, represented by the instant when, on the pressure gauging curve, first a pressure drop of at least 14 kPa (2 psi) over 15 minutes, and then, over the next 15 minutes, another drop of at least 14 kPa (2 psi) take place.

[0028] The induction time is determined by the time elapsed from the test start (positioning of the bomb inside the heating bath) to the break point.

[0029] Apparently, the induction time is a direct expression of the gasoline liability to gum formation during storage. This evaluation parameter is highly significant for highly unstable gasolines, like the cracked ones.

EXAMPLE 1.

[0030] Effectiveness of the TBC (tert.butyl-catechol) + PNTZ (phenothiazine) blend with respect to the stabilizers of the prior art.

[0031] The induction time for a series of stabilizers used in the art, including that of TBC and PNTZ, each individually, and that of TBC+PNTZ blends in different ratios, is measured for comparison on a cracked gasoline (Gasoline 1, Bromine number 65, diene value 7). The results are reported in the following Table 1.

TABLE 1

PRODUCT SAMPLE	DOSAGE (ppm)	INDUCTION TIME (min)
Blank		60
Irganox 1010	300	180
2,6-DTB-phenol	300	195
PDA	150	330
TBC	150	300
2,4-DM-6-TB-phenol	150	180

TABLE 1 (continued)

PRODUCT SAMPLE	DOSAGE (ppm)	INDUCTION TIME (min)
PNTZ	150	190
TBC+PNTZ	75+75	360
TBC+PNTZ	100+50	400
TBC+PNTZ	50+100	330

[0032] The table shows the predictable result that, when used individually, the best products are the PDA and the TBC, in accordance to long-time refinery practice. However, surprisingly, the blend TBC+PNTZ according to the invention emerges as a stabilizer having an effectiveness even greater than that of the PDA, therefore being capable of replacing the latter with improvement of performance, as well as toxicity elimination.

EXAMPLE 2.

[0033] A test series was carried out in order to assess the optimal ratio between the two components of the TBC+PNTZ blend, on the basis of the induction time method. The results are reported in the following Table 2.

TABLE 2

PHENOTHIAZINE (ppm)	TBC (ppm)	INDUCTION TIME (min)
0	150	300
75	75	360
150	0	190
37.5	112.5	375
50	100	400
60	90	390

[0034] Tests results, reported on a curve, show that the best stabilization is provided by a weight ratio of about 2:1 between the two components TBC and PNTZ (TBC 66.66% and phenothiazine 33.33%) with a <400 min induction time value.

EXAMPLE 3.

[0035] The effectiveness of a 1:2 PNTZ+TBC blend is directly compared to that of the PDA, always with reference to the induction time, for a cracked gasoline (Gasoline 2, Bromine number 62, diene value 8). The results are reported in the following Table 3.

TABLE 3

STABILIZER	DOSAGE (ppm)	Induction Time (min)
Blank		60
PDA	75	225
PNTZ+TBC	50	240
PDA	100	255
PNTZ+TBC	100	300
PDA	125	300
PNTZ+TBC	150	405
PDA	175	315
PNTZ+TBC	200	435
PDA	200	315

[0036] As it is apparent from the results reported in Table 3, the dosage (quantity in ppm) of the additive according to the invention and of the PDA, the stabilizing effectiveness (induction time) is significantly higher for the blend of the present invention, and this under extremely less critical operative conditions.

EXAMPLE 4

[0037] The partial PDA replacement with tert.butyl phenols (TBP) was advanced in the prior art, in order to reduce the environmental risks. Table 4 shows some results obtained on two types of cracked gasolines of the prior art, in which the addition of the above-mentioned tert.butyl-phenols (TBP) appears to be substantially effective, since, in the PDA replacement, the effectiveness of the former proves to be substantially equal to the PDA one. Therefore, the advantage of the TBPs is that of approximately obtaining the same effects of the PDA, yet with a 50% decrease of the latter, and with the entailed reduction of the toxicity hazards.

[0038] The results are reported in the following Table 4.

TABLE 4

STABILIZER	Dosage (ppm)	PDA content (ppm)	Induction Time (min)
Gasoline 3 Br. N° 40 diene value 2	-	-	45
PDA/TBP 1:1	200	100	435
PDA	200	200	435
PDA/TBP 1:1	500	250	720
PDA	500	500	735
Gasoline 4 Br n° 62 diene value 8	-	-	45
PDA/TBP 1:1	300	150	400
PDA	300	300	400
PDA	200	200	360
PDA	100	100	240

[0039] The above-reported results are compared to those of the following Table 5, wherein the induction time values measured under the same conditions of Table 4 are compared to the induction time values obtained by the additive of the present invention, for the stabilizing effectiveness of the same gasoline type and for different gasolines.

Gasoline 5	Br N° 56	diene value 4
Gasoline 6	Br N° 58	diene value 5
Gasoline 7	Br N° 40	diene value 3
Gasoline 8	Br N° 62	diene value 9

TABLE 5

Gasoline Sample	STABILIZER	INDUCTION TIME (min)
Gasoline 5	PDA/TBP 1:1 (90 ppm)	180
	PNTZ/TBC (30 ppm)	150
	PDA/TBP 1:1 (180 ppm)	315
	PNTZ/TBC (60 ppm)	285
Gasoline 6	PDA/TBP 1:1 (180 ppm)	300
	PNTZ/TBC (60 ppm)	300

TABLE 5 (continued)

Gasoline Sample	STABILIZER	INDUCTION TIME (min)
	PDA/TBP 1:1 (270 ppm)	435
	PNTZ/TBC (90 ppm)	435
Gasoline 7	PDA/TBP 1:1 (90 ppm)	165
	PNTZ/TBC (30 ppm)	165
	PDA/TBP 1:1 (235 ppm)	375
	PNTZ/TBC (75 ppm)	360
Gasoline 8	PDA/TBP 1:1 (270 ppm)	375
	PNTZ/TBC (30 ppm)	375
	PDA/TBP 1:1 (360 ppm)	420
	PNTZ/TBC (120 ppm)	420

[0040] The test results reported in Table 5 should be compared to those of Table 4. They refer to tests carried out in order to simulate a wide range of cracked products, with gasoline characteristics, like, e.g. the Bromine number and the diene value, differing thereamong. This tests prove that the blend PNTZ/TBC of the present invention can replace, even with a higher effectiveness, the PDA+TBP blends, completely avoiding any toxicity hazard deriving from the use of the aromatic amines.

[0041] As in the above, the induction time test is applied also in the following examples 5-9, in which the effectiveness of the additive according to the invention (PNTZ-TBC in a 1:2 ratio) is compared to that of other stabilizers of the known art. The test is carried out on gasolines outputted by various industrial FCC (Fluid Catalytic Cracking) plants located in various European countries.

EXAMPLE 5

[0042] The first gasoline sample is made of 26% C5 hydrocarbon cut, 60% light gasoline and 14% medium gasoline.

Cut characteristics:		
	Light gasoline	Medium gasoline
Density	0.680	0.780
P.I.	35°C	71°C
50% vol.	56°C	143°C
95% vol.	110°C	195°C
P.F.	139°C	213°C
Br N°	92 gr./100 cc	40 gr./100 cc
Sulfur	120 ppm	630 ppm
Olefins	44% p	27.4% p
Paraffins	46.9% p	34.3% p
Naphtens	5.4% p	13.5% p
Aromatics	3.7% p	24.7% p
Blank Induction Time: 75 min.		

Dosage	PNTZ + TBC (1:2)	TBC + 2,6 DTB Phenol (1:4)	PDA + 2,6 DTB Phenol (1:1)
3 ppm	315'		
6 ppm		225'	
7.5 ppm	480'		

(continued)

Dosage	PNTZ + TBC (1:2)	TBC + 2,6 DTB Phenol (1:4)	PDA + 2,6 DTB Phenol (1:1)
9 ppm			495'
15 ppm	570'	240'	
30 ppm		300'	
45 ppm		480'	

EXAMPLE 6.

[0043] The second gasoline sample has the following characteristics.

Cut characteristics:	
Density	0.678
P.I.	32°C
50% vol.	54°C
95% vol.	106°C
P.F.	124°C
Br N°	91.5 gr./100 cc
Sulfur	96 ppm
Olefins	32.5% p
Paraffins	58.5% p
Naphtenes	6.1% p
Aromatics	2.9% p
Blank Induction Time: 75 min.	

Dosage	PNTZ + TBC (1:2)	TBC + 2,6 DTB Phenol (1:4)	PDA + 2,6 DTB Phenol (1:1)	2,6 DTB Phenol + 2,4 DM 6, TB Phenol (7:1)
7.5 ppm	400'			
15 ppm	630'	325'		
20 ppm			340'	285'
30 ppm		415'		
40 ppm				360'
45 ppm			555'	

EXAMPLE 7.

[0044] The third sample has the following characteristics.

Cut characteristics:	
Density	0.7217
P.I.	35°C
5% vol.	45°C
10% vol.	50°C
30% vol.	62°C
50% vol.	79°C

(continued)

Cut characteristics:	
90% vol.	140°C
95% vol.	150°C
P.F.	165°C
Sulfur	0.08% p
Blank Induction Time: 188 min.	

Dosage	PNTZ + TBC (1:2)	PDA + 2,6 DTB Phenol (1:1)
3 ppm	225'	
7.5 ppm	>520'	
9 ppm		207'
22.5 ppm		>520'

EXAMPLE 8.

[0045] The fourth sample is a light gasoline having the following characteristics.

Cut characteristics:	
Density	0.6638
P.I.	30°C
5% vol.	36°C
50% vol.	51°C
95% vol.	95°C
P.F.	144°C
Blank Induction Time: 180 min.	

Dosage	PNTZ + TBC (1:2)	PDA + 2,6 DTB Phenol (1:1)
15 ppm	870'	
45 ppm		555'

EXAMPLE 9.

[0046] The fifth sample is a medium gasoline having the following characteristics.

Cut characteristics:	
Density	0.7582
P.I.	87°C
5% vol.	97°C
50% vol.	110°C
95% vol.	139°C
P.F.	147°C
Blank Induction Time: 90 min.	

Dosage	PNTZ + TBC (1:2)	PDA + 2,6 DTB Phenol (1:1)
15 ppm	400'	
45 ppm		285'

EXAMPLE 10.

[0047] Another test battery was carried out using a different ASTM test method, always related to the gasoline stability, carried out on a gasoline sample additioned with 100 ppm stabilizer, stored at 40°C for 43 days in a blanketed flask.

[0048] The so-called existent gums, i.e. the quantity of polymers formed (in mg/100 ml gasoline) following a brisk evaporation of a gasoline quantity in a preheated air jet at 160-165 °C, are determined through the ASTM D381/94 method, entitled «Standard test method for existent gum in fuels by Jet Evaporation».

[0049] Carrying out the same method on specimens of the gasoline stored at 40°C, additioned and not, at T=0 and at day 8, 22, 29 and 43 an increasing trend of said quantity of formed polymers (gums) is observed, which evidently is inversely proportional to the stabilizing effectiveness of the added additive.

[0050] In fact, the effectiveness of the product is inversely proportional to the quantity of gums to be found. This difference in the effectiveness is already apparent at T=0, i.e., when the ASTM D381 test is carried out right after the additioning, because the additive prevents the gum formation during the hot evaporation provided by the method itself. However, the significance of such difference of effectiveness increases over time. In fact, the additive prevents the gum formation during the storage at 40°C.

[0051] The results in mg/100 ml of a cracked gasoline sample are the following:

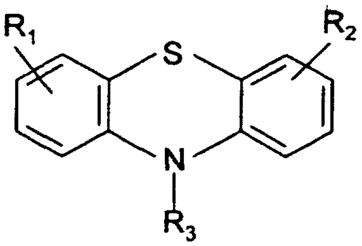
	days	0	8	22	29	43
Blank		834	746	804	1595	3891
PDA	100 ppm	717	536	561	862	2639
PNTZ + TBC (3:2)	100 ppm	698	469	555	722	2525

[0052] The above-reported result, obtained during and after the 43-day period, evidences a higher effectiveness of the PNTZ-TBC blend with respect to the aromatic amine, associated to an absence of toxicity, by virtue of the absence of the aromatic amines.

Claims

1. The use of a gasoline stabilizing composition for inhibiting a gasoline degradation by preventing gum formation in said gasoline, wherein said stabilizing composition comprises as effective inhibition ingredients:

A) substituted or unsubstituted phenothiazine (PNTZ) of formula

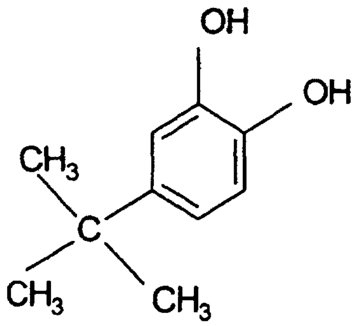


formula (1)

wherein R_1 and R_2 represent H, alkyl C_1-C_{20} and cycloalkyl C_5-C_{20} groups and R_3 represents H, alkyl C_1-C_{20} and cycloalkyl C_5 - C_{20} or phenyl groups, said alkyl and cycloalkyl groups possibly containing functional groups,

or dimer phenothiazine and

B) tert.butyl-catechol (TBC) of formula

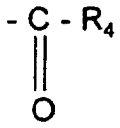


formula (2)

in a ratio of 5:95 to 80:20 therebetween.

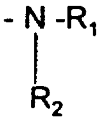
2. The use according to claim 1, wherein said functional groups are selected from the class comprising:

esther or carboxylic acid groups and derivatives thereof, of the type



$$-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-R_4$$

wherein R_4 is H, OH, R_3, $-OR_1$, or $-OR_3$;
alcohol or esther groups of the $-O-R_3$ type;
amino groups of the type



$$-\underset{\displaystyle R_2}{\underset{|}{N}}-R_1$$

or mercaptane or sulfur groups of the $-S-R_1$ type.

3. The use according to claim 1 or 2, wherein said ratio is 27:75 to 40:60.

4. The use according to any one of the preceding claims, wherein said ratio is 30:70 to 35:65.

5. The use according to any one of the preceding claims, wherein said gasoline is a gasoline produced by a cracking process.

6. The use according to claim 5, wherein said cracking process is a steam cracking process.

7. The use according to claim 5, wherein said cracking process is a thermal cracking process.

8. The use according to claim 5, wherein said cracking process is a catalytic cracking process.

9. The use according to any one of the preceding claims, further comprising usual PNTZ- and TBC-compatible carriers.

10. A stabilized gasoline comprising a gasoline and a stabilizing composition as claimed in any one of the claims 1 to 9 in an amount effective to inhibiting a gasoline degradation by preventing gum formation in said gasoline.

11. The stabilized gasoline according to claim 10, wherein said gasoline is a gasoline produced by a cracking process.

12. The stabilized gasoline according to claim 11, wherein said cracking process is a steam cracking process.

13. The stabilized gasoline according to claim 11, wherein said cracking process is a thermal cracking process.

14. The stabilized gasoline according to claim 11, wherein said cracking process is a catalytic cracking process.

15. The stabilized gasoline according to claim 10, wherein said effective composition quantity is 5 to 1000 ppm.

16. The stabilized gasoline according to any one of claims 10 to 15, wherein the ratio between phenothiazine and tert. butyl-catechol is 5:95 to 80:20.

17. The stabilized gasoline according to claim 16, wherein said ratio is 27:75 to 40:60

18. The stabilized gasoline according to claim 17 wherein said ratio is 30:70 to 35:65.

19. The stabilized gasoline according to any one of the claims 10 to 18, further comprising usual PNTZ- and TBC-compatible additives and carriers.

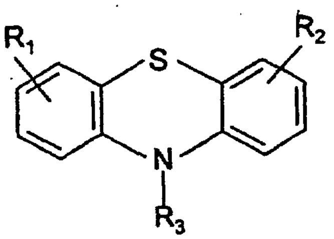
20. A method of stabilizing a gasoline for inhibiting a degradation thereof by preventing gum formation in said gasoline, comprising the step of adding to said gasoline an effective amount of a stabilizing composition as claimed in claim 1.

21. The method of stabilizing a gasoline according to claim 20, wherein said effective amount is 5 to 1000 ppm.

Patentansprüche

1. Die Verwendung einer Benzin-stabilisierenden Zusammensetzung zur Hemmung einer Zersetzung von Benzin durch Verhinderung der Bildung von Gummi in besagtem Benzin, wobei besagte stabilisierende Zusammensetzung als wirksame hemmende Inhaltsstoffe:

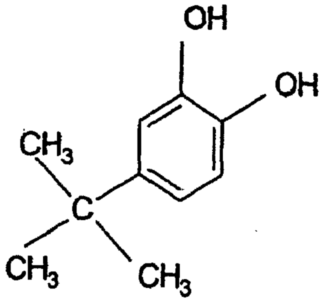
A) substituiertes oder unsubstituiertes Phenothiazin (PNTZ) der Formel



Formel (I)

worin R_1 und R_2 H, C_1-C_{20}-Alkyl- und C_5-C_{20}-Cycloalkyl-Gruppen darstellen und R_3 H, C_1-C_{20}-Alkyl- und C_5-C_{20}-Cycloalkyl- oder Phenyl-Gruppen darstellt, wobei besagte Alkyl- und Cycloalkyl-Gruppen möglicherweise funktionelle Gruppen enthalten, oder dimeres Phenothiazin und

B) tert.-Butyl-catechol (TBC) der Formel

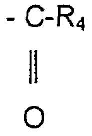


Formel (2)

in einem Verhältnis untereinander von 5 : 95 bis 80 : 20 umfasst.

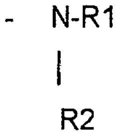
2. Die Verwendung gemäß Anspruch 1, worin besagte funktionelle Gruppen aus der Gruppe ausgewählt sind, die:

Ester- oder Carbonsäure-Gruppen und Derivate hiervon, vom Typ



$$-\underset{\underset{\displaystyle O}{\|}}{C}\text{-}R_4$$

worin R_4 H, OH, R_3, $-OR_1$, oder$-OR_3$ ist;
Alkohol- oder Ester-Gruppen vom $-O-R_3$-Typ;
Amino-Gruppen vom Typ



$$-\underset{\underset{\displaystyle R2}{|}}{N}\text{-}R1$$

oder Mercaptan- oder Schwefel-Gruppen vom Typ $-S-R_1$ umfasst.

3. Die Verwendung gemäß Anspruch 1 oder 2, worin besagtes Verhältnis 27 : 75 bis 40 : 60 beträgt.

4. Die Verwendung gemäß einem der vorhergehenden Ansprüche, worin besagtes Verhältnis 30 : 70 bis 35 : 65 beträgt.

5. Die Verwendung gemäß einem der vorhergehenden Ansprüche, worin besagtes Benzin ein Benzin ist, das durch ein Cracking-Verfahren hergestellt wurde.

6. Die Verwendung gemäß Anspruch 5, worin besagtes Cracking-Verfahren ein Steam-Cracking-Verfahren ist.

7. Die Verwendung gemäß Anspruch 5, worin besagtes Cracking-Verfahren ein thermisches Cracking-Verfahren ist.

8. Die Verwendung gemäß Anspruch 5, worin besagtes Cracking-Verfahren ein katalytisches Cracking-Verfahren ist.

9. Die Verwendung gemäß einem der vorhergehenden Ansprüche, die zusätzlich übliche PNTZ- und TBC-verträgliche Träger umfasst.

10. Ein stabilisiertes Benzin, das ein Benzin und eine stabilisierende Zusammensetzung, wie sie in einem der Ansprüche 1 bis 9 beansprucht wird, in einer Menge, die wirksam ist, um eine Benzinzersetzung durch Verhinderung der Bildung von Gummi in besagtem Benzin zu hemmen, umfasst.

11. Das stabilisierte Benzin gemäß Anspruch 10, worin besagtes Benzin ein Benzin ist, das durch ein Cracking-Verfahren hergestellt wurde.

12. Das stabilisierte Benzin gemäß Anspruch 11, worin besagtes Cracking-Verfahren ein Steam-Cracking-Verfahren ist.

13. Das stabilisierte Benzin gemäß Anspruch 11, worin besagtes Cracking-Verfahren ein thermisches Cracking-Verfahren ist.

14. Das stabilisierte Benzin gemäß Anspruch 11, worin besagtes Cracking-Verfahren ein katalytisches Cracking-Verfahren ist.

15. Das stabilisierte Benzin gemäß Anspruch 10, worin die Menge der besagten wirksamen Zusammensetzung 5 bis 1000 ppm beträgt.

16. Das stabilisierte Benzin gemäß einem der Ansprüche 10 bis 15, worin das Verhältnis zwischen Phenothiazin und tert-Butyl-catechol 5 : 95 bis 80 : 20 beträgt.

17. Das stabilisierte Benzin gemäß Anspruch 16, worin besagtes Verhältnis 27 : 75 bis 40 : 60 beträgt.

18. Das stabilisierte Benzin gemäß Anspruch 17, worin besagtes Verhältnis 30 : 70 bis 35 : 65 beträgt.

19. Das stabilisierte Benzin gemäß einem der Ansprüche 10 bis 18, das zusätzlich übliche PNTZ- und TBC-verträgliche Additive und Träger umfasst.

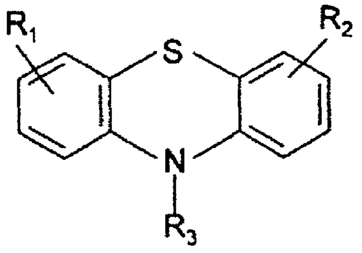
20. Ein Verfahren zur Stabilisierung eines Benzins zur Hemmung seiner Zersetzung durch die Verhinderung der Bildung von Gummi in besagtem Benzin, das den Schritt der Zugabe einer wirksamen Menge einer stabilisierenden Zusammensetzung, wie sie in Anspruch 1 beansprucht wird, umfasst.

21. Das Verfahren zur Stabilisierung eines Benzins gemäß Anspruch 20, worin besagte wirksame Menge 5 bis 1000 ppm beträgt.

Revendications

1. Utilisation d'une composition stabilisant l'essence pour inhiber une dégradation de l'essence en évitant la formation de gomme dans ladite essence, dans laquelle ladite composition stabilisante comprend en tant qu'ingrédient efficace d'inhibition :

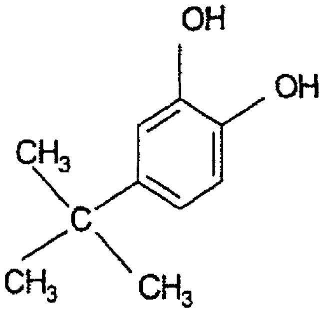
A) une phénothiazine (PNTZ) substituée ou non substituée de la formule



formule (1)

dans laquelle R_1 et R_2 représentent H, des groupes alkyle en C_1 à C_{20} et des groupes cycloalkyle en C_5 à C_{20}, et R_3 représente H, des groupes alkyle en C_1 à C_{20} et cycloalkyle en C_5 à C_{20} ou bien phényle, lesdits groupes alkyle et cycloalkyle contenant facultativement des groupes fonctionnels, ou une phénothiazine dimère et

B) du tert.butyl-catéchol (TBC) de formule

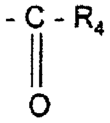


formule (2)

selon un rapport de 5:95 à 80:20 entre eux.

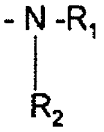
2. Utilisation selon la revendication 1, dans laquelle lesdits groupes fonctionnels sont choisis dans la classe comprenant :

   des groupes ester ou acide carboxylique et des dérivés de ceux-ci, du type



$$-\underset{\substack{\| \\ O}}{C}-R_4$$

dans laquelle
R_4 est H, OH, R_3, $-OR_1$ ou $-OR_3$;
des groupes alcool ou ester du type $-O-R_3$;
des groupes amino du type



$$-\underset{\substack{| \\ R_2}}{N}-R_1$$

ou des groupes mercaptan ou soufre du type $-S-R_1$.

3. Utilisation selon la revendication 1 ou 2, dans laquelle ledit rapport est de 27:75 à 40:60.

4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle ledit rapport est de 30 :70 à 35 : 65.

5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle ladite essence est une essence produite par un procédé de craquage.

6. Utilisation selon la revendication 5, dans laquelle ledit procédé de craquage est un procédé de craquage à la vapeur.

7. Utilisation selon la revendication 5, dans laquelle ledit procédé de craquage est un procédé de craquage thermique.

8. Utilisation selon la revendication 5, dans laquelle ledit procédé de craquage est un procédé de craquage catalytique.

9. Utilisation selon l'une quelconque des revendications précédentes, comprenant en outre des supports habituels

compatibles avec PNTZ et TBC.

10. Essence stabilisée comprenant une essence et une composition stabilisante telle que revendiquée dans l'une quelconque des revendications 1 à 9 en une quantité efficace pour inhiber une dégradation de l'essence en évitant une formation de gomme dans ladite essence.

11. Essence stabilisée selon la revendication 10, dans laquelle ladite essence est une essence produite par un procédé de craquage.

12. Essence stabilisée selon la revendication 11, dans laquelle ledit procédé de craquage est un procédé de craquage à la vapeur.

13. Essence stabilisée selon la revendication 11, dans laquelle ledit procédé de craquage est un procédé de craquage thermique.

14. Essence stabilisée selon la revendication 11, dans laquelle ledit procédé de craquage est un procédé de craquage catalytique.

15. Essence stabilisée selon la revendication 10 dans laquelle ladite quantité de composition efficace est de 5 à 1000 ppm.

16. Essence stabilisée selon l'une quelconque des revendications 10 à 15, dans laquelle le rapport entre la phénothiazine et le tert.butyl-catéchol est de 5:95 à 80:20.

17. Essence stabilisée selon la revendication 16, dans laquelle ledit rapport est de 27:75 à 40:60.

18. Essence stabilisée selon la revendication 17, dans laquelle ledit rapport est de 30:70 à 35:65.

19. Essence stabilisée selon l'une quelconque des revendications 10 à 18, comprenant en outre des additifs et des supports habituels compatibles avec PNTZ et TBC.

20. Un procédé de stabilisation d'une essence pour inhiber une dégradation de celle-ci en évitant la formation de gomme dans ladite essence, comprenant l'étape d'ajouter à ladite essence une quantité efficace d'une composition stabilisante telle que revendiquée dans la revendication 1.

21. Procédé pour stabiliser une essence selon la revendication 20, dans lequel ladite quantité efficace est de 5 à 1000 ppm.