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STABILIZED HYDROCARBONS

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7 Claims. (Cl. 44-9)

My invention relates to stabilized hydrocarbons and has particular reference to stabilized petroleum distillates, such as cracked gasoline containing unsaturated hydrocarbons.

The object of my invention is to provide substances which, when added in small quantities to hydrocarbons and, in particular, to reformed gasoline, retard or even prevent their deterioration in storage for a long period of time.

As is known, gasoline obtained by cracking so-called heavy petroleum oils, considerably changes its properties when kept in storage. Such changes affect the value of gasoline as a motor fuel and often render it entirely unsuitable for this purpose.

In the following disclosure, all substances which stabilize reformed (cracked) gasoline will be called, for brevity's sake, inhibitors.

A thorough study of the chemical nature and structure of gasoline inhibitors led me to the discovery of certain rules permit prediction of the chemical structure of substances having valuable inhibiting properties.

One of these rules may be formulated as follows: the most active inhibitors have properties of photographic developers. In connection with the law of quinones, disclosed in my patent application Serial No. 31,623, filed July 16, 1936, the other rule may be formulated as follows: aromatic compounds, having in their molecule active groups and able to be converted into corresponding quinones upon oxidation, stabilize gasoline, i. e., have practically valuable inhibiting properties.

Photographic developers reduce very rapidly, under certain conditions, light-sensitive silver salts after their exposure to light. Under identical conditions they remain for a long time entirely passive to the unexposed silver salts.

The inhibiting action of agents which reduce unexposed silver salts is extremely brief: they become rapidly oxidized by air and then cease to act as inhibitors. If, however, a certain reducing agent remains passive to the light-sensitive silver salts even after their exposure to light, then such substance will prove to be practically void of inhibiting properties.

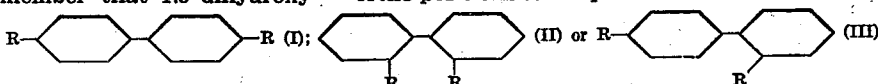
My rules are confirmed, first, by the chemical structure of all the hitherto known inhibitors. It will suffice to remember that 1,5-dihydroxy-

developer. I was able to show, however, that this substance, in complete agreement with my law herein called inhibitor-developers, has developing properties and, consequently, it confirms the above mentioned rule, which unites the majority of active inhibitors into one characteristic general family of chemical substances. This rule will be hereinafter called the "rule of developers-inhibitors". I firmly established this rule by direct and very broad experimental research. For this purpose I used all of the photographic developers which I discovered and described for the first time in my patent application Serial No. 31,623, filed July 16, 1935. The chemical structure of these developers does not correspond to the rules set forth by Lumiere Brothers and Seyewitz, also by Andresen (A. H. Dietz, The Theory of Developing, p. 17, 1922, D. Van Nostrand Co., New York). They have been found by applying my law of quinones as explained in the copending application mentioned.

It was impossible to predict a priori that these peculiar developers will be also practically valuable inhibitors stabilizing reformed gasoline. Experiments have shown however, that in this case also, the substances having developing properties are at the same time inhibitors.

These substances differ from other developers-inhibitors by their relative stability, and they also excel by the correspondingly longer duration of their effect in both cases, as photographic developers, and as inhibitors extending the life of reformed gasoline, being more stable under action of a moist air and pure oxygen.

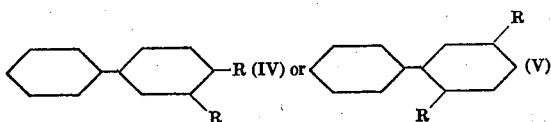
Inhibitors of this class which I discovered represent binuclear compounds the nucleus of which is of an aromatic character. Each of its two nuclei must have at least one active (salt-forming) group, these groups being only hydroxyl (OH), amino-group (NH₂), or imino-group (NH). The active groups of all these compounds must be located in the nuclei of the binuclears in such a manner, that they must be able to form corresponding quinones upon oxidation and the nucleus so substituted is "quinonizable". Thus, in particular, if a binuclear contains in each of its nuclei only one active group, then these groups may occupy para-para, ortho-ortho, or para-ortho positions to the place of union of the nuclei:



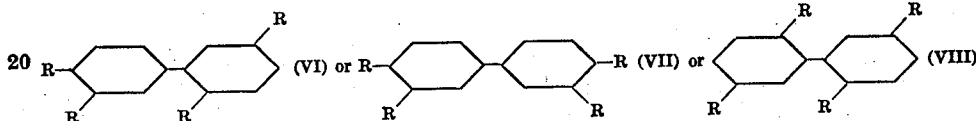
naphtalin has not been studied as a photographic

where R denotes active groups.

If, however, both active groups are located in the same nucleus of a binuclear, then they may occupy in relation to each other any but meta positions, for instance:



Finally, if each nucleus of a binuclear has two active groups, then the last mentioned rule must be applied to at least one pair of active groups: they in this case may occupy para or ortho, but not meta positions to each other. It is evident, of course, that with the following arrangement of each of the two pairs of active groups:



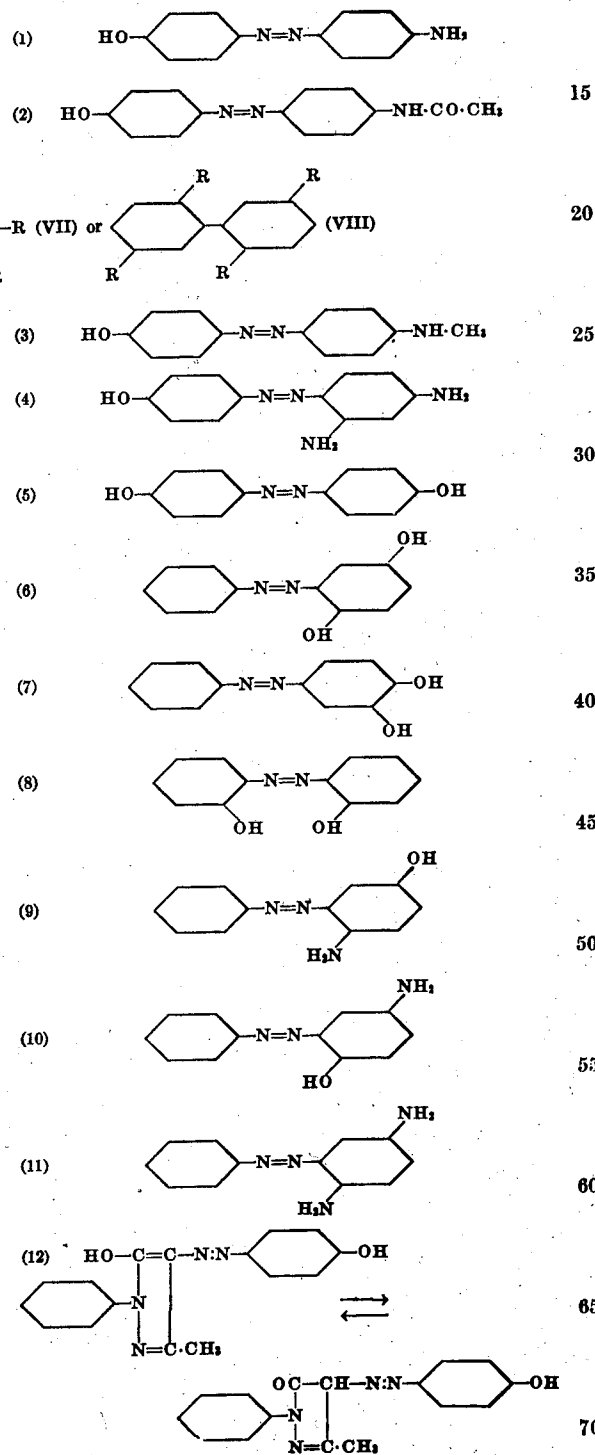
the corresponding inhibitors have relatively greater activity: stabilization of cracked gasoline in this case may be effected with a reduced quantity of the inhibitor. Benzene nuclei in the Formulas I to VIII may be replaced by other nuclei having clearly expressed aromatic character and, in particular, by the nuclei of naphthalene, anthracene, pyridine, quinoline, isoquinoline, pyrrole, thiophene, furfuran, cyclopentadiene, and other similar nuclei. It is understood, that one or more hydrogen atoms of these nuclei may be replaced by any radicals and, in particular, by alkyl-, acyl-, and alkoxy-groups, nitro-group, halogens, etc. My stabilizers can be expressed by the following general formula: $X-R-(M)_n-R'-Y$, where n is an integral number, M may be an alkylene, sulfide (or sulfur), azo, hydrazo, Schiff's base group and the like, R may be pyridine, quinoline, pyrrole, furfuran, thiophene, cyclopentadiene, pyrazolone, or an aromatic hydrocarbon, preferably of a relatively low molecular weight (in order to have a greater proportion of active or ionizable hydrogen), whose ring hydrogen is substituted by X in the quinonizable position, such, for instance, as positions 2 or 4 in the hydrocarbon ring, and X is one or more active radicals from the group consisting of OH, NH_2 and NH ; R' may be also one of the nuclei listed for R and having its ring hydrogen substituted by Y , the latter being one or more OH radicals in the quinonizable position such as 2 or 4 in the hydrocarbon ring. Y may be the one of the X groups, however, in cases when R and R' are connected by radical bridges, i. e. when n is more than 1.

The following inhibitors are especially valuable by their ability to retain their effectiveness for a relatively long time: 4,4'-dihydroxy-diphenyl, 3,3'-dimethyl-4,4'-dihydroxy-diphenyl, 4-hydroxy-4'-amino-diphenyl, 4-hydroxy-4'-acetylamino-diphenyl, 3,5,3',5'-tetramethoxy-4,4'-dihydroxy-diphenyl (known as hydrocoerulignon).

The binuclear developers discovered by me do not lose their developing properties even if their nuclei are connected together not directly, but by certain radicals (bridges), such as azo- and hydrazo-groups ($-N:N-$), ($-NH.NH-$), ethene-bridge ($-CH:CH-$), sulfide radical ($-S-$), etc. Experiments have shown that also in this case the corresponding compounds function as developing agents if they can be converted into corresponding biquinones by oxidation,

It was impossible to predict a priori whether substances of this new class of developers will have inhibiting properties. Experiments have proved, however, that my rule is valid also in this case. In other words, experiments have proved that the new developers of a peculiar group have very valuable inhibiting properties.

I have investigated more particularly the following azo-inhibitors:

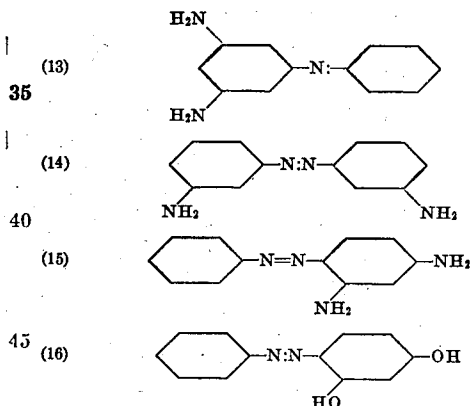


The compound (12), 1-phenyl-3-methyl-5-pyrazolone-4-azo-para-hydroxy-benzene, has not been described in the literature. It is obtained by coupling of diazotized para-amino-

phenol with phenyl-methyl-pyrazolone, preferably in an alkali solution. It represents a powder of an orange color, which can be recrystallized from methyl alcohol, or xylol, or from ethyl acetate. When heated in a capillary, this substance melts, after preliminary sintering, at the temperature of about 207° C. It then decomposes and grows in volume.

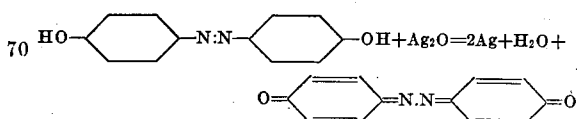
Developing properties of the compounds 6 to 11 inclusive could be predicted, as these compounds must be considered as complex derivatives of the known developers, i. e., hydroquinone, para-aminophenol, para-phenylenediamine, and para-acetylaminophenol. It was impossible, however, to predict inhibiting properties for these developers. Experiments have shown that the entrance of the aryl-azo group into the aryl nucleus of the already known developers stabilizes the latter in relation to the action of moist air, i. e., converts these developers into more stable compounds without affecting their valuable inhibiting properties. As a result, these azo-compounds have relatively more valuable inhibiting properties, because they produce stabilizing effect on unsaturated hydrocarbons for a relatively longer time.

Unlike the foregoing 12 azo-compounds and their analogues relatively to the position of the active groups, the following substances are practically valueless as inhibitors:



In complete agreement with my rule of inhibitors-developers, experiments have shown that these substances are passive to the light-sensitive silver salts before and after their exposure.

Further experiments have explained this fact and led me to the formulation of the following general rule: developing properties and, consequently, properties of sufficiently active and, therefore, practically very valuable inhibitors, exist in such azo-compounds only, the active groups of which are located in the molecule in such manner that it can be converted into the molecule of a corresponding quinone upon oxidation. For example, 4,4'-dihydroxy-azobenzene readily oxidizes, according to Willstaetter and Benz (Berichte Der Deutscher Chemische Gesellschaft, v. 39, p. 3482, 1906), into the corresponding quinone under action of silver oxide, according to the equation:

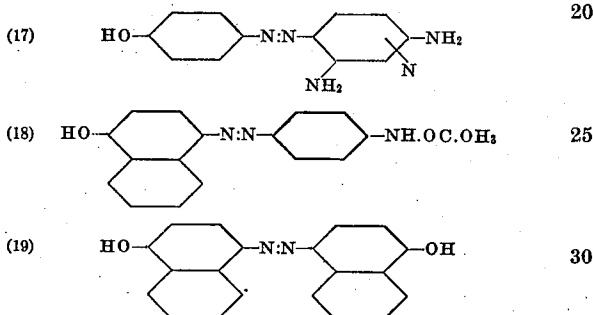


In accordance with its ability to be converted into the corresponding quinone, this azo-compound

has also both, developing and inhibiting properties.

The foregoing compounds, from (13) to (16) inclusive, on the contrary, cannot form quinones or quinonimines, because their active groups are located in meta positions to each other or to the azo-group, serving as a bridge in the molecule. In accordance with the lack of ability to form corresponding quinones or quinonimines upon oxidation, the compounds from (13) to (16) inclusive have no developing properties, and their inhibiting properties, expressed, for instance, by the cyclohexene number, are also relatively insignificant.

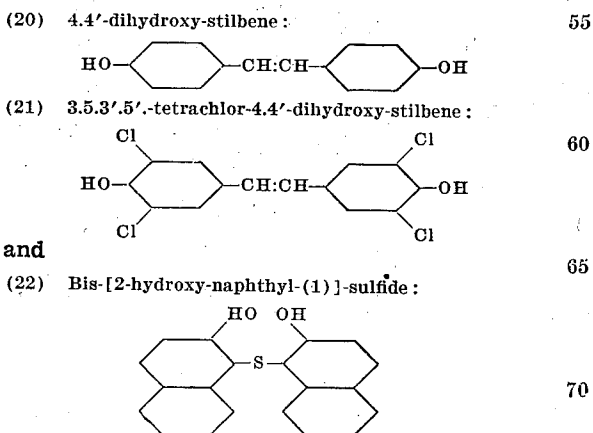
Benzene nuclei of the azo-compounds can be replaced by other radicals of an aromatic character and, in particular, by such groups as naphthyl, pyridyl, quinolyl, etc. Incidentally, I have thoroughly studied the following azo-compounds:



Each of these compounds (17, 18 and 19) proved to have properties of photographic developers and, at the same time, as it should be, expected in accordance with the rule of developers-inhibitors, also very valuable inhibiting properties.

In the following disclosure, for brevity's sake, the term "aryl groups" will be used to denote all cyclic radicals of an aromatic character, such as the nuclei of anthracene, phenanthrene, pyrene, pyridine, quinoline, isiquinoline, pyrrole, thiophene, furfuran, cyclopentadiene, pyrazolin, and other similar radicals.

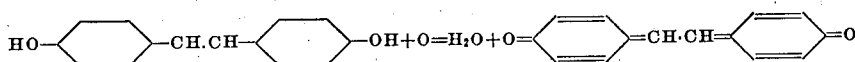
Further experiments have shown that the azo-group in azo-inhibitors can be replaced not only by the analogous hydrazo-group, but also by a number of other radical-bridges, in particular by ethene-group ($-\text{CH}:\text{CH}-$) and sulphur atom ($-\text{S}-$), i. e., by the sulfide radical. Thus, for instance, I succeeded in discovering active inhibiting properties in the following compounds:



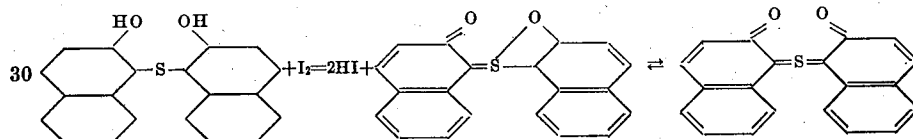
The question as to which of the radical-bridges is suitable for replacing the azo-group in azo-inhibitors in order to produce new compounds,

also having inhibiting properties, is solved by the same method as the question of the positions of the active groups.

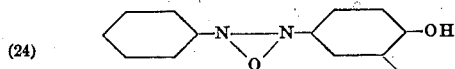
Both of these problems present themselves in a case when each aryl radical of a given compound has only one active group. In such case the azo-group can be replaced by such radicals only which permit the conversion of resulting compounds into corresponding quinones upon oxidation. This is because only with such replacement will the new compounds have developing properties and, therefore, will also act as powerful inhibitors. It is understood, of course, that the active groups of such compounds in this case may occupy only positions 4.4', 2.2' and 4.2', as only with such positions of the active groups a given substance can be oxidized into a corresponding quinone. Thus, in particular, active inhibitors Nos. 20, 21 and 22, become readily converted into corresponding quinones upon oxidation, for example:



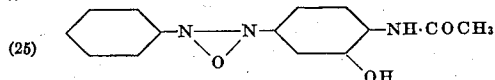
25 (Zinke and Muench *Annalen der Chemie*, v. 335, p. 157, 1904), and, according to Hinsberg:



Upon replacement of the azo-group in azo-inhibitors by the azoxy-group, substances are obtained having inhibiting properties only if their molecule has at least two active groups, and if both these groups are located on the same aryl nucleus in para or ortho positions in relation to each other. In particular, the compounds:



45 and



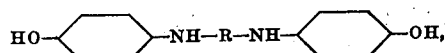
50 have very valuable inhibiting properties.

A large number of my inhibitors readily dissolve in cracked gasoline, directly and sufficiently quickly, but each of them can be easily introduced in gasoline, without any admixtures, but as a solution in benzene, xylol, alcohols, and, especially, in ketones, such as acetone, methyl-ethylketone, etc., in which almost all azo-dyes dissolve very well and almost instantaneously, even at the room temperature.

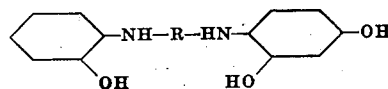
Superior solubility of various coloring substances, including azo-dyes, when mixed with hydroxy-benzenes, must be explained by the ability of these coloring substances to form with hydroxy-benzenes corresponding salts or so-called double compounds.

The law of quinones predicts which particular radicals may be replaced by one hydrogen atom in the amino-group in order to obtain a product which, like the original, will have developing properties. In particular, this law predicts that all binuclear compounds, each nucleus of which, having one hydroxyl group and one imino-group in para or ortho position to each other, connected together by nitrogen of the imino-group and radicals of the general formula: C_nH_{2n} or $\text{C}_n\text{H}_{2n+2}$,

etc., possess developing properties. This is because each of the substances:



or:

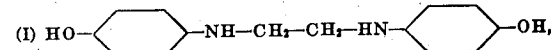


where R represents a radical consisting only of the atoms of carbon and hydrogen, becomes readily converted into corresponding quinones upon oxidation.

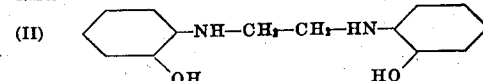
Direct experiments have shown that all these compounds have also very valuable inhibiting properties. Consequently, my rule of developers-inhibitors extends also to these complex compounds.

In particular, I studied more thoroughly the action of two isomeric (di-hydroxyphenylimino)-

ethanes, i. e., ortho-ortho- and para-para-isomers:



and



I obtained all these substances by direct heating of a corresponding amino-phenol (para or ortho) with ethylenechloride, preferably with the excess of the latter. The heating can be conducted in an autoclave, as well as in an open vessel with a reflux condenser. Actual tests have shown that both these substances have very valuable inhibiting as well as developing properties.

Further experiments have shown that if a developer-inhibitor contains in its molecule an amido-group, it may be rendered more active as an inhibitor if one molecule of benzaldehyde is added to one or two molecules of my amido-inhibitor; the length of time of the action of such mixture on reformed gasoline is also noticeably increased. It is possible, of course, to use as inhibitors corresponding compounds of benzaldehyde (Schiff's bases) in chemically pure state, although such compounds, when added to wet gasoline, become dissociated, at least partially, into free benzaldehyde and corresponding amido-inhibitors.

It appears that the increase of activity of the foregoing inhibitors as observed in presence of benzaldehyde, can be explained by the ability of the latter substance to become oxidized in presence of amino-inhibitors into benzoic acid thereby acting itself to a certain extent as an inhibitor.

Comparative studies of my inhibitors, described in this specification, with reference to the inhibitors already known in the literature, have been conducted by the copper dish method, by

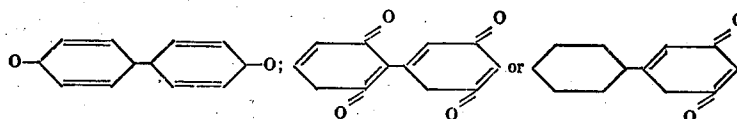
the styrol and cyclohexane number, and, also, by the method of oxidation of gasoline in an autoclave in pure oxygen under high pressure, determining the induction period by the observed decrease in pressure.

A large majority of these inhibitors directly dissolve in reformed gasoline. In some cases it is advisable to prepare a separate solution of an inhibitor in acetone, methylethylketone, etc., and then add this solution to gasoline.

By taking into consideration molecular weight of my inhibitors and the number of active groups

These binuclears have in the side chain of each nucleus at least one active group having ionizable hydrogen atom. These active groups impart to the compounds of the aromatic series one of their most important characteristic properties, i. e. the property to become quinonized.

Quinonized binuclear compounds retain their cyclic nuclei unchanged, at least in the first stage of oxidation but the active groups split off their hydrogen atoms, leading to the formation of binuclear mono and diquinones (di- or tetra-ketones or ketoimines) such as:



in each of their nuclei, I was able to determine their weight equivalents corresponding to an equal or almost equal effect on gasoline. As a rule, the theoretical determination agreed with the results of tests.

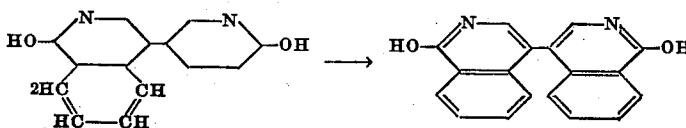
With reference to the molecular weight it should be noted that compounds having nuclei of relatively high molecular weight, when they exceed 125, for instance, are of little practical value since their active or ionizable hydrogen atoms, essential for the stabilizing action, form but a small percentage of the total weight of the substance.

The simplest quinonizable compounds are cyclic unsaturated compounds of the aromatic character

The position of double bonds becomes in this case changed and their number is reduced for mono and diquinones by one or two respectively.

It is understood that the formation of quinones is possible only for certain positions of the active groups as described above.

Polycyclic binuclears may be considered as derivatives of the simplest binuclears each of whose two cyclic nuclei of the aromatic character has only 5 or 6 carbon atoms. Their nuclei have bivalent radicals C_nH_{2n} or C_nH_{2n-2} as their side chains, as, for example, alpha-alpha-biquinolyl may be considered as 4,4'-dihydroxy-dipyridyl whose each nucleus has, as a side chain, the radical of Δ -1,3-butadiene: $-CH:CH:CH:CH-$

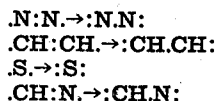


ter whose nucleus has only 5 or 6 carbon atoms and 3 or 2 double bonds arranged in the so-called conjugated double bonds. These compounds may be iso or heterocyclic. In the side chains of these simplest compounds, i. e. in positions 1 and 2 or 1 and 4, there must be present at least two groups containing ionizable hydrogen. These groups are usually called "active groups" and include amino-, imino-groups and hydroxyl.

Quinonizable compounds retain their cyclic nucleus unchanged, at least in the first stage of oxidation, but they split off two hydrogen atoms from their active groups, being converted into corresponding quinones or quinoid compounds, i. e. unsaturated cyclic diketones or keto-imines 1.2 or 1.4 of the aliphatic character; simultaneously in the nuclei of the quinonized compounds the number of double bonds is reduced by one and they change their positions, namely, in the nuclei of the simplest quinones or quinoid compounds the conjugated double bonds are absent.

The quinonizable binuclears described above are compounds having in each of the two cyclic nuclei of the aromatic character 5 or 6 carbon atoms and 3 or 2 double bonds arranged in conjugated double bonds. These compounds may belong either to iso or heterocyclic classes of organic compounds:

It is understood that in cases when nuclei of these binuclears are connected together by the radical-bridges, these radicals must be of such composition and structure as not to prevent the quinonization, as disclosed above. Out of all the known radicals I have found only four radicals suitable for quinonization. These radicals change the position of their bonds in this process as follows:

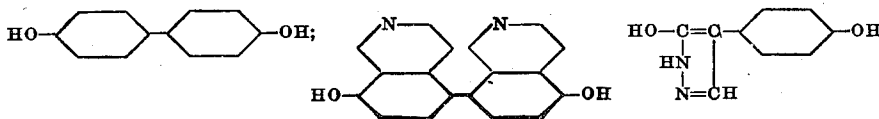


Reformed gasoline which has been kept in storage for a more or less extended period of time requires for the stabilization of its ethylene compounds relatively greater quantities of inhibitors of a given group than a freshly prepared gasoline. Similar phenomenon is observed with the stabilization of certain chemically pure oils, such as styrol and cyclohexene.

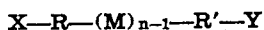
Usually it is necessary to add from about 0.001% to not more than about 0.5% of these inhibitors to gasoline for its stabilization.

I claim as my invention:

1. A cracked gasoline stabilized by addition

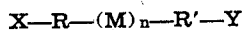


thereto of a small quantity of a compound having the formula:



5 where M is selected from the class consisting of alkylene, sulphur, azo, hydrazo, Schiff's base group, n is an integral number, R is an aromatic hydrocarbon nucleus of molecular weight less than 125, pyridine, quinoline, pyrrole, furfuran, 10 thiophen, pyrazolone, whose ring hydrogen is substituted by X in a quinonizable position such as 2 or 4 or both in the hydrocarbon ring, and X is one or more active radicals taken from the class consisting of OH, NH and NH_2 ; R' is an 15 aromatic hydrocarbon nucleus of molecular weight less than 125, pyridine, quinoline, pyrrole, furfuran, thiophen, pyrazolone, which may be the same or different from R and whose ring hydrogen is substituted by Y which is one or 20 more OH radicals in the quinonizable position such as 2 or 4 or both on the hydrocarbon ring.

2. An unsaturated hydrocarbon tending to oxidize and form gummy substances, stabilized by the addition thereto of a small quantity of a 25 compound having the formula:



where M is selected from the class consisting of alkylene, sulphur, azo, hydrazo, Schiff's base 30 group, n is an integral number, R and R' are aromatic hydrocarbon nuclei of molecular weight

less than 125 each, pyridine, quinoline, pyrrole, furfuran, thiophen, pyrazolone, whose ring hydrogens have been substituted by X and Y in the quinonizable position such as 2 or 4 or both in the hydrocarbon ring, X and Y are each one or 5 more active radicals taken from the class consisting of OH, NH and NH_2 .

3. A cracked gasoline stabilized by adding thereto a small quantity of a compound as set forth in claim 1, characterized in that the hydrocarbon nucleus of the compound is taken from the class consisting of benzene and cyclopentadiene nuclei. 10

4. An unsaturated hydrocarbon tending to oxidize and form gummy substances, stabilized by addition thereto of a small quantity of 4'-hydroxyphenylazo-(1-phenyl-3-methyl)-pyrazolone. 15

5. An unsaturated hydrocarbon tending to oxidize and form gummy substances stabilized by addition thereto of a small quantity of 4,4'-dihydroxy-3,3'-dimethyldiphenyl. 20

6. An unsaturated hydrocarbon tending to oxidize and form gummy substances, stabilized by addition thereto of a small quantity of 2',4'-(alpha-alpha)-4-hydroxyphenylazo-diaminopyridine. 25

7. A method of stabilizing cracked gasoline, consisting in adding thereto a small quantity of a substance as set forth in claim 1. 30

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