Role of Pyrroles in Fuel Instability

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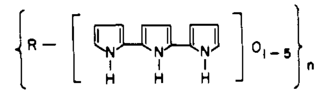
THE ADVERSE effect of pyrroles on the color stability and cleanliness of petroleum distillates is known but not satisfactorily understood. By this work, the authors attempt to clarify the type of chemical reactions involved in color and sediment formation by pyrroles. Experiments were carried out in pure hydrocarbon solutions containing alkylpyrroles and other color and sediment precursors. To exaggerate their effects, the concentrations of these precursors were usually much higher than in petroleum distillates.

Pyrroles and peroxides were found to produce colored, polymeric residues. Acyl peroxides reacted with pyrrole immediately yielding sediments of the "pyrrole black" type with the following tentative formula

where

R = organic radical from the reactant with pyrrole.



(1)

Hydroperoxides were less active but also produced colored deposits of high nitrogen content in hydrocarbons containing pyrroles. If mercaptans were also present in such hydrocarbon solutions in addition to pyrrole and the hydroperoxide, the sediments formed were black, heavier, less soluble, and contained up to one atom of sulfur per three atoms of nitrogen.

Hydroperoxides containing sulfur from mercaptan-olefin co-oxidation are generally more reactive than hydrocarbon hydroperoxides toward pyrrole, but their reaction is limited because of rearrangement to hydroxyethyl sulfoxides. The latter compounds also react with pyrrole although at a slower rate.

The results of this work indicate that the formation and decomposition of hydroperoxides may be important in the precipitation of pyrrole type compounds from petroleum products.

CRACKED PETROLEUM

Distillates containing aromatic thiols and olefins are very susceptible to air oxidation. Aromatic thiols are readily co-oxidized with reactive olefins by molecular oxygen; hydroperoxides containing sulfur are formed (*18*).

$$AR{-}SH + CHR{=}CR'_2 + O_2 \rightarrow Ar{-}S{-}CHR{-}CR'_2{-}O_2H$$

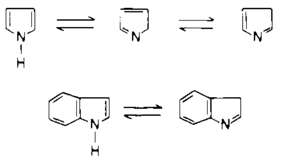
Oswald and Rupar (*18, 20*) suggested that the effect of aromatic thiols on the stability of catalytically cracked gas oils is mainly due to mercaptan-olefin co-oxidation. However, the organic sediments formed in petroleum distillates contain high percentages of nitrogen as well as sulfur. An attempt was made to explain the latter fact by studying the reactions of pyrrolic nitrogen compounds with hydroperoxides and their decomposition products.

LITERATURE REVIEW

Heterocyclic compounds containing a five-membered ring with one nitrogen are found in small quantities in petroleum products. These compounds—pyrroles, indoles, carbazoles—can be all regarded as pyrrole derivatives. In petroleum fractions, the alkylated derivatives are the common components (*9, 27*). According to Sauer and others, the pyrroles and indoles in domestic heating oil distillates are mostly mono- and dialkyl substituted with two to three carbon atoms in the alkyl groups.

Pyrrole-type nitrogen compounds are largely responsible for color formation in cracked gas oils (*13*). The oxidation of pyrroles results in the formation of gum in shale oil naphtha (*10*). According to Thompson and others (*29*), pyrrole-type compounds act as primary sludge formers in fuel oil. Sludges recovered from line filters to domestic oil burners invariably show high percentages of nitrogen. 2-Naphthalenesulfonic acid was isolated after 3 months' storage at 110° F. from a catalytically cracked fuel oil in which the original thiols had been replaced by an equivalent amount of 2-naphthalenethiol (*17*). Such sulfonic acids may precipitate the pyrroles of petroleum. Sauer, Weed, and Headington (*28*) suggested that in heating oil blends, thiols catalyze the side chain oxidation of reactive hydrocarbons, nitrogen and sulfur compounds present primarily in the catalytically cracked component, to form hydroperoxides. The latter, in part, end up as condensed esterified high molecular weight products in the form of sediments.

The effect of pyrroles on color and sediment formation in fuels is connected with their oxidation and polymerization reactions (Table I). Pyrrole oxidation by molecular oxygen probably involves peroxide intermediates. C-alkylated pyrroles and indoles are easier to oxidize than the parent compounds. N-alkylated pyrroles are relatively stable towards air oxidation. Therefore, the ease of autoxidation of pyrroles with NH groups is probably related to their tautomerization to form pyrrolenines.



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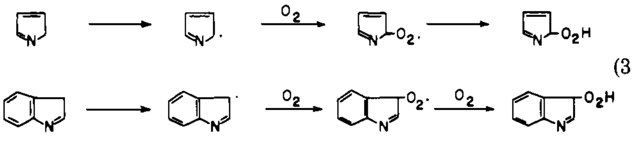
Starting from α-pyrrolenine and β-indolenine, respectively, the following autoxidation schemes are suggested:



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In the case of alkylated pyrrole derivatives, hydrogen abstraction from the side chain is also possible (*11*). Many pyrroles give poorly defined polymeric substances on oxidation. Such substances were named "pyrrole blacks" by Angeli (*3*). A number of these pyrrole blacks were obtained by Italian researchers (*3, 4, 5, 23*) by different oxidants mostly in acidic media.

In acidic media pyrroles oxidize faster. Hydrochloric acid trimerizes pyrrole (*24*) and dimerizes monoalkylpyrroles and indole (*1, 14*). Dialkylpyrroles with one substituent on each side of the ring are even more sensitive to acids and yield condensation products of unknown structure that have lost one mole of ammonia for every two moles of pyrrole (*1*). The reaction of pyrroles with oxygen and/or acids often leads to the rupture of the pyrrole ring (*6*). Finally, the condensation of pyrroles with aldehydes and ketones (*12*) can also result in the formation of polymers.

EXPERIMENTAL METHODS

In a study of these reactions in relation to fuel instability, experiments were carried out in our laboratory with hydro-

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carbon solutions of pyrroles to determine the type of reactions producing color and sediment. Storage experiments were usually carried out in open borosilicate glass flasks at 110° F. (43° C.) and 210° F. (99° C.). Special emphasis was placed on investigating the effect of mercaptan-olefin co-oxidation on the color stability of hydrocarbons containing pyrroles. The pyrroles used were commercially available compounds: pyrrole, 2,5-dimethylpyrrole, 2,4-dimethyl-3-ethylpyrrole, *N*-butylpyrrole, indole, and 2,3-dimethylindole. Petroleum distillates of most concern contain higher boiling pyrrole derivatives than the above compounds. The concentrations of these and sulfur compound precursors were usually much higher than in petroleum distillates.

EFFECT OF HYDROCARBON AND MERCAPTAN TYPES ON PYRROLE OXIDATION

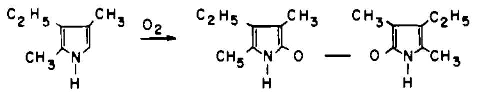
Pure hydrocarbons (cetane, xylene, tetrahydronaphthalene), major hydrocarbon types present in petroleum distillates, were used as solvents for pyrrole and mercaptans expected to be color and sediment precursors. About 300 ml. of the solutions of these compounds were stored in open 500-ml. borosilicate glass Erlenmeyer flasks. Changes in the color of the solutions were observed and measured on the Saybolt (Say.) or Tag-Robinson (Rob.) scales. The weight of sediment formed was determined after filtration, *n*-heptane wash, and drying at 210° F. (Table II).

Pyrrole alone did not cause additional color or sediment

Table I. Oxidation and Polymerization Reactions of Pyrrole-Type Compounds

Isolated peroxide intermediates of autoxidation of substituted pyrroles.

Reference



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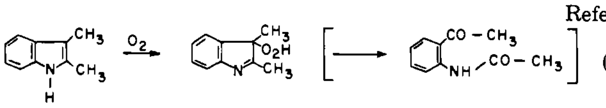

Reference

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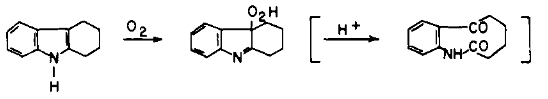

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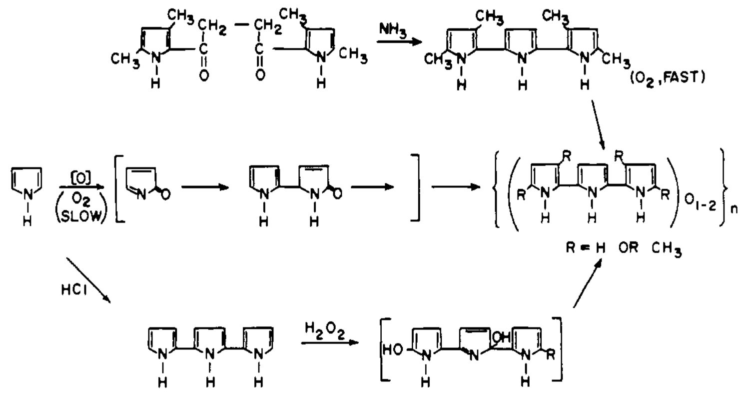
Suggested routes to and structure of pyrrole black polymers



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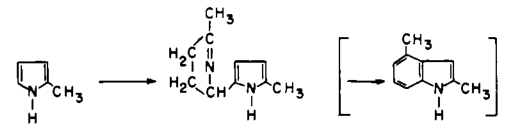
(4, 22)

(21)

Dimerization of pyrroles and indoles



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Suggested scheme of polycondensation of pyrrole with aldehydes and ketones

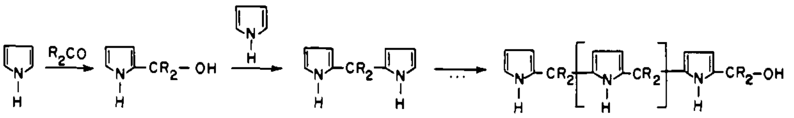

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Table II. Effect of Hydrocarbons on Pyrrole and Mercaptan Stability

(6 weeks' storage at 110° F.)

			In Cetane		In Xylene		In Tetrahydronaphthalene	
Pyrrole, Mole/L.	Mercaptan Added	Mole/L.	Color	Sediment, mg./100 ml.	Color	Sediment, mg./100 ml.	Color	Sediment, mg./100 ml.
Nil	...	Nil	+29 Say.	0.2	+18 Say.	0	+6 Say.	0
0.3	...	Nil	+28 Say.	0	...	0	+23 Say.	0
Nil	Benzenethiol	0.3	+26 Say.	0.1	+21 Say.	...	Too dark	201
0.15	Benzenethiol	0.15	+16 Say.	0	...	...	Too dark	880
Nil	2-Naphthalenethiol	0.3	25 Rob.	0	18.5 Rob.	0	...	...
0.15	2-Naphthalenethiol	0.15	21 Rob.	0	10 Rob.	14.5	...	...
Nil	*tert*-Dodecanethiol	0.3	+23 Say.	0.5	2 Rob.	6	1 Rob.	660
0.15	*tert*-Dodecanethiol	0.15	17 Rob.	2.5	2 Rob.	2.5	Too dark	1560

formation in any of the hydrocarbon solvents. When pyrrole and a mercaptan were both present, generally more color loss and heavier sediment were observed than in the presence of the thiol only. Color and sediment formation in different hydrocarbon solutions of mercaptans depends very much on the hydrocarbon type. For example, cetane solution of *tert*-dodecanethiol hardly changes in storage at 110° F., while in tetrahydronaphthalene it forms a dark mixture with heavy sediment. The increase in sediment caused by the presence of pyrrole in such solutions also depends on the hydrocarbon solvent. In cetane, color loss and sediment formation are low, but in tetrahydronaphthalene, both effects are significant. In tetrahydronaphthalene containing pyrrole, *tert*-dodecanethiol produced more sediment than any of the other mercaptans examined. This sediment contained 9% nitrogen.

Pyrroles, reportedly, have a greater adverse effect on the stability of catalytically cracked gas oil than virgin gas oil. An interaction between olefins and pyrrole in the presence of air may be one possible explanation for this difference. This assumption was to some extent supported by storage experiments in pure cetane containing olefins and pyrrole (Table III).

The results show that olefins in the presence of pyrrole cause more color loss and sediment formation than in the absence of pyrrole. None of the test solutions became acidic.

The effect of both saturated and olefinic hydrocarbons on the precipitation of pyrroles is probably due to their radical and peroxide-forming tendency on oxidation.

REACTION OF HYDROCARBON PEROXIDES WITH PYRROLES

Some experiments of Angeli (*3*) and other Italian researchers (*23*) on the formation of pyrrole black were carried out with aqueous hydrogen peroxide and pyrrole dissolved in acetic acid. The formation of pyrrole black in these experiments was apparently caused by peracetic acid which is formed by the reaction of hydrogen peroxide with acetic acid.

To determine if pyrrole black type polymers play a part in the formation of oil deposits, pyrrole black formation in pure hydrocarbons was studied. Peracids and acyl peroxides reacted with pyrrole immediately, yielding a black sediment. When a benzene solution (50 ml.) of benzoyl peroxide (0.05 mole) was left standing for 3 days at room temperature, a heavy black sediment formed. This sediment was filtered, washed with benzene and naphtha (50 ml. each), then extracted twice with 500 ml. of boiling water for 20 minutes. An elemental analysis of the 1.5 grams of remaining residue indicated the composition, $C_{19}H_{12}O_4N_3$. (Found C, 64.82; H, 3.79; N, 12.1. Calculated: C, 65.54; H, 4.01; N, 12.1.) On the basis of this composition and the work of Pieroni and Moggi (*22*), the following pyrrole black formula is suggested for this polymer:

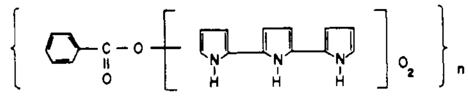
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Table III. Effect of Olefins on Stability of Pyrrole Solutions

(4 weeks' storage at 110° F. in cetane)

Added Compd., 0.3 Mole/L. Olefin	Pyrrole	Color	Sediment, Mg./100 Ml.
Nil	Yes	+28 Say.	0
n-Octadecene	No	+18 Say.	0
	Yes	18.5 Rob.	3.2
Cyclohexene	No	+30 Say.	0
	Yes	+28 Say.	1.2
Styrene	No	+20 Say.	Turbidity
	Yes	+26 Say.	3
Dipentene	No	+10 Say.	90.3
	Yes	19.5 Rob.	183.5 (5.5% N)

Work with other acyl peroxides (4-chlorobenzoyl peroxide and 2,4-dichlorobenzoyl peroxide) has shown similar results. The presence of chlorine in the black sediments indicated the presence of chlorobenzoyl groups. When *tert*-dodecanethiol was present in addition to pyrrole in the benzene solution, the sediment resulting after the addition of benzoyl peroxide contained about 1% sulfur and 9% nitrogen.

Hydrocarbon hydroperoxides react with pyrrole at a much slower rate than acyl peroxides. When 4 grams of *tert*-butyl hydroperoxide–bis-*tert*-butyl peroxide mixture (*16*) was added to 26.8 grams (0.4 mole) of pyrrole, no immediate reaction took place. When the reaction mixture was heated on a steam bath, the mixture gradually turned dark red in 4 hours. After the volatile components were distilled off at 10-mm. pressure on a steam bath, 10 grams of red viscous residue remained. Further vacuum distillation of this residue yielded 4.5 grams of yellow viscous liquid boiling at 90–1° C. at 2 mm. This liquid had n_D^{20} 1.5079 and the following composition: C, 57.83; H, 8.14; N, 12.8. Characteristic parts of its infrared spectrum are shown in Figure 1. On standing, this liquid turned red and became more viscous, was soluble in water, and gave a neutral reaction with litmus. The residue from vacuum distillation was a brownish powder, readily soluble in water. Attempts to identify these substances were unsuccessful.

In another exploratory experiment, the effect of cumene hydroperoxide on sediment formation was studied in benzene solutions at 110° F. Pyrrole and mercaptans were present in addition to the peroxide as sediment precursors. Data in Table IV show that the benzene solution containing pyrrole and cumene hydroperoxide produced a large amount of sediment with high nitrogen content. Similarly, *tert*-dodecanethiol and the hydroperoxide yielded a heavy sediment containing 11.7% sulfur. However, when both pyrrole and thiol were present in the hydroperoxide solution, the amount of sediment was much higher. All the solutions were acidic. It is possible that the pyrrole ring was oxidatively cleaved in a manner similar to dimethylindole and tetrahydrocarbazole (Table I, *6, 30*).

The effect of hydroperoxides on sediment formation was also examined in the presence of 2,5-dimethylpyrrole and 2,3-dimethylindole. These pyrrole derivatives, more sensitive to oxidation (*26*), produced some sediment and color

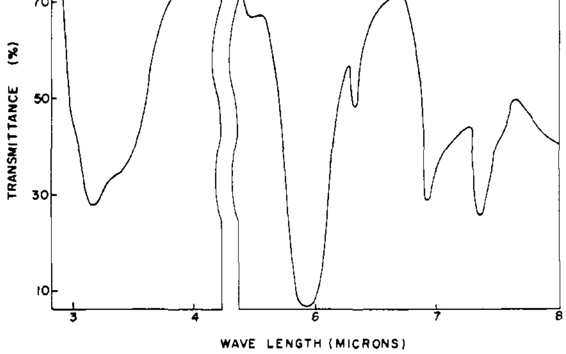


Figure 1. Infrared spectrum of the product of pyrrole–butyl hydroperoxide reaction
(b.p. 90–1° at 2 mm.)

even in the absence of hydroperoxides. The added hydroperoxides, however, produced much heavier sediments, especially in the presence of mercaptans.

N-substituted pyrroles, 1-phenyl- and 1-butylpyrrole, were relatively unreactive with hydroperoxides.

The results of the experiments with hydroperoxides and pyrrole show the formation of sediments insoluble in hydrocarbons and having properties similar to pyrrole blacks. In the presence of both pyrrole and mercaptan, the action of the hydroperoxide resulted in formation of highly insoluble polymers containing up to one sulfur atom for each three of nitrogen. Infrared spectra of these materials in pyridine solution and in Paraffinol suspension showed strong absorption peaks at about 3.1 and 5.9 microns corresponding to NH or OH and to CO groups. Absorption peaks were also observed between 8 and 10 microns; these were more characteristic of a sulfone group than a sulfide or sulfoxide.

It is possible that the mercaptans were oxidized to sulfonic acids and the latter precipitated the pyrrole to form these sulfur-containing pyrrole blacks, as suggested by Offenhauer, Brennan, and Miller (*17*). However, it is probable that the pyrrole was attacked by the radical intermediates of mercaptan oxidation, because the oxidation of mercaptans to sulfonic acids is too slow a process to explain the high percentage of sulfur in the sediments formed.

REACTION OF PYRROLES WITH OLEFIN MERCAPTAN CO-OXIDATION PRODUCTS

Reactive olefins and mercaptans co-oxidize in hydrocarbon solutions in the presence of air to form substituted mercaptoethyl hydroperoxides (*18, 20*).

$$(\mathrm{R{-}SH} \rightarrow \mathrm{RS}\cdot)$$

$$\mathrm{R{-}S}\cdot + \mathrm{CHR'{=}CR_2''} \rightarrow \mathrm{R{-}S{-}CHR'{-}CR_2''}\cdot$$

$$\mathrm{R{-}S{-}CHR'{-}CR_2''}\cdot + \mathrm{O_2} \rightarrow \mathrm{R{-}S{-}CHR'{-}CR_2''{-}O_2}\cdot$$

$$\mathrm{R{-}S{-}CHR'CR_2''{-}O_2}\cdot + \mathrm{RSH} \rightarrow \mathrm{R{-}S{-}CHR'{-}CR_2''{-}O_2H} + \mathrm{RS}\cdot$$

These hydroperoxides rearrange on standing at room temperature to substituted 2-hydroxyethyl sulfoxides:

$$\mathrm{R{-}S{-}CHR'{-}CR_2''{-}O_2H} \rightarrow \mathrm{R{-}SO{-}CHR'{-}CR_2''{-}OH}$$

On the co-oxidation of α-methylstyrene with 2-naphthalenethiol (2-hydroperoxy-2-phenyl)-propyl 2-naphthyl sulfide is formed according to the above mechanism.

This hydroperoxide was added to pyrrole in benzene and tetrahydronaphthalene solutions. The loss in color, sediment formed, and acidity are shown in Table V.

According to these data, the mixture containing hydroperoxide and pyrrole in benzene produced a severe color loss and a large amount of pyrrole black type sediment containing 7.4% nitrogen and 7.4% sulfur. On cooling and filtering, a large quantity of the crystalline hydroxyethyl sulfoxide was obtained. The mixture containing the hydroperoxide alone yielding an even larger amount of hydroxyethyl sulfoxide. The solutions containing the hydroperoxides have shown some acidity, possibly as a result of hydroperoxide decomposition.

A reaction between sulfur-containing hydroperoxides and pyrrole in hydrocarbon solution might be better carried out if the former compounds are formed in situ by mercaptan-olefin co-oxidation.

An alkylated pyrrole, 2,5-dimethylpyrrole, sensitive to peroxide attack, was aerated at 0° C. in 100 ml. of *n*-heptane solution in the presence of thiophenol and styrene, each in 0.3 mole per liter concentration. After 5½ hours' reaction time, a yellow viscous oil started to separate from the mixture. After 17 hours' aeration, the heterogeneous reaction mixture was cooled in an acetone–dry ice mixture when 2.7 grams of bright red oil separated. This oil was freed from volatile components by purging it with N_2 under 1-mm. pressure at 25° C. It did not contain any peroxide. An analysis of the residue has shown: C, 73.92; H, 7.11; N, 3.64; S, 10.07; 0 (by difference) 5.26. The infrared spectrum of this product is shown in Figure 2. This spectrum shows absorption peaks characteristic of a $\mathrm{{-}CO{-}N{=}}$ group at about 5.9 microns. In this respect, this spectrum is somewhat similar to the spectrum of butyl hydroperoxide–pyrrole reaction product in Figure 1. Both spectra show that the oxidized pyrrole polymers may have carbonyl groups adjacent to the pyrrolic nitrogen.

Similar aeration experiments at 0° C. were carried out with solutions containing pyrrole, thiophenol, and styrene or pyrrole, thiophenol, and indene. These solutions also precipitated colored oils after 5½ hours. These oils had a

Table IV. Effect of Cumene Hydroperoxide on Stability of Solutions Containing Pyrrole and Mercaptans

(2 weeks' storage at 110° F. in benzene solutions containing 0.33 mole/l. cumene hydroperoxide)

Added Compound, Mole/L.			Color,	Sediment		
Mercaptan		Pyrrole	Rob.	Mg./100 ml.	S, %	N, %
Nil	...	Nil	>25	0	...	...
	...	1	10.5	487	...	13.4
tert-Dodec-	0.33	Nil	1.5	208	12.9	...
anethiol	0.33	1	[a]	1682	5.0	11.7
Benzene-	0.33	Nil	3.5	5	...	...
thiol	0.33	1	[a]	401	7.7	10.1

[a] Too dark.

Table V. Effect of Pyrrole and Hydroperoxides from Mercaptan-Olefin Co-oxidation on Stability of Pyrrole Solutions

(16 hours' storage at 110° F.)

Added Compd., 0.3 Mole/L.						
(2-Hydroperoxy-2-phenyl)-propyl 2-naphthyl sulfide	Pyrrole	Solvent	Color, Rob.	Sediment, Mg./100 Ml.	Acid Number	Hydroxy-Sulfoxide[a], Mg./100 Ml.
No	Yes	Benzene	>25	0	...	...
Yes	No		9	0	0.5	2500[c]
Yes	Yes		0	582[b]	0.5	1900[c]
No	Yes	Tetrahydro-naphthalene	25	0	...	...
Yes	No		13	0	...	...
Yes	Yes		0.5	150	0.2	...

[a] Crystallized on cooling filtrate. [b] Contained 7.4% nitrogen and 7.4% sulfur. [c] Both had melting point of 115–118° C. and were identical. Anal. Calcd. for 2-hydroxy-2-phenylpropyl 2-naphthyl sulfoxide, $C_{19}H_{15}O_2S$: C, 73.52; H, 5.84; S. 10.3. Found: C, 72.80; H, 5.85; S, 10.2.

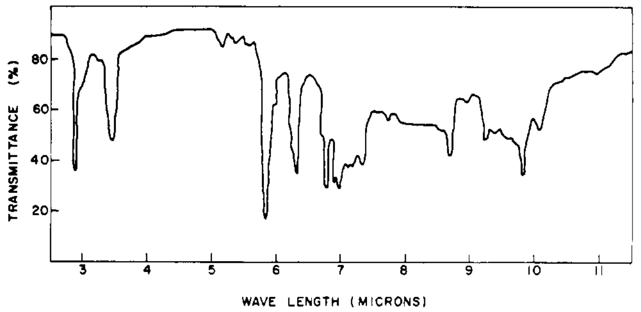


Figure 2. Infrared spectrum of product of thiophenol, styrene, and 2,5-dimethylpyrrole co-oxidation at 0° C.

lower nitrogen content, probably because pyrrole is less sensitive to peroxide attack than 2,5-dimethylpyrrole. Aeration experiments at room temperature gave similar results. Lower (0.01 mole per liter) concentrations of pyrroles also produced minor amounts of reddish precipitates in the presence of mercaptans and olefins (each 0.01 mole per liter) in 24 hours.

In further experiments with pyrroles, the importance of interaction with mercaptans and olefins during storage in the presence of air was examined. Cetane solutions of pyrrole, olefins, and thiophenol were stored and then examined for color loss, acidity, and sediment (Table VI). All solutions with pyrrole showed color loss and precipitated black sediment, generally less than in similar solutions not containing pyrrole. However, the color loss in the presence of pyrrole was more severe. Solutions containing pyrrole and reactive olefin-type structures (styrene, indene) tended to produce more sediment than those containing *n*-α-olefins. An elemental analysis of the sediments formed in the presence of pyrrole revealed the presence of 6.1 and 3.9% nitrogen. The lower nitrogen contents, compared to those obtained with pyrrole blacks from the direct oxidation with hydrocarbon hydroperoxides, suggest that co-oxidation reactions not involving pyrroles were also occurring. The corresponding hydroxysulfoxide co-oxidation product crystallized from the filtrates of test solutions containing thiophenol, pyrrole, and indene (styrene) on standing. None of the solutions were acidic.

The effect of thiophenol-styrene co-oxidation was also examined on alkylated pyrroles and alkylated indoles at 0.3 mole per liter precursor concentration. The results obtained with alkylpyrroles are shown in Table VII.

The addition of styrene or thiophenol to 2,5-dimethylpyrrole did not increase the amount of sediment formed; even had a stabilizing effect. However, when all three components (thiophenol, styrene, and dimethylpyrrole) were present, the solution became red within 2 hours. The heavy sediment formed in this solution contains C, 70.17; H, 7.17; N, 10.9; S, 6.70; 0 (by difference), 15.96.

Similar experiments with 2,4-dimethyl-3-ethylpyrrole and 2,3-dimethylindole gave similar results. However, 2,3-dimethylindole was so prone to oxidation by air that the presence of thiophenol and styrene caused no definite difference in sediment formation. When *N*-substituted pyrroles (*N*-phenyl- and *N*-butylpyrrole) were used in the accelerated storage experiments in cetane, only the solutions containing both thiophenol and styrene had changed and formed sediment after one month. These sediments contained only 1.6 and 0.4% nitrogen, respectively. These data suggest that the *N*-substituted pyrroles had no active part in sediment formation.

A short study was made to determine the effect of aliphatic mercaptans, which are less active than aromatic thiols, on the stability of cetane solutions of pyrrole and olefins. Storage experiments (Table VIII) again show rapid color loss and sediment formation in all solutions containing pyrrole.

Table VI. Mercaptan-Olefin Co-oxidation in Presence of Pyrrole

(Storage at 110° F. in cetane solutions containing 0.3 mole/l. thiophenol)

Olefin		Pyrrole, Mole/L.	Storage Period, Days	Color, Rob.	Sediment		
	Mole/l.				Mg./100 ml.	S, %	N, %
n-Octadecene	0.3	Nil	28	25	1000	8.5[a]	...
	0.3	0.3	28	2	50	...	...
Styrene	0.3	Nil	14	25	4.2	...	...
	0.3	0.3	14	18	55.7	...	6.1
Indene	0.6	Nil	5	25	1800	11.1[a]	...
	0.6	0.3	5	...	200	9.5	3.9

[a] Sulfur value found on analyzing pure hydrosulfoxide obtained by recrystallization of sediment.

Table VII. Mercaptan-Olefin Co-oxidation in Presence of Alkylated Pyrroles

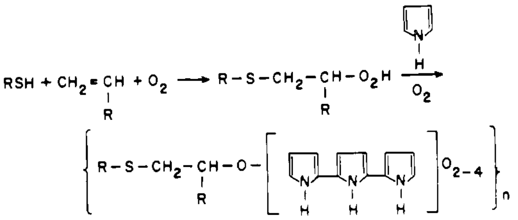
(Storage at 110° F. in cetane solvent)

Added Compd., 0.3 Mole/L.			Appearance[b]		Determinations after 24 Hr.		
Alkylated pyrrole[a]	Styrene	Thiophenol	After 2 hr.	After 24 hr.	Color, Rob.	Sediment[c] mg./100 ml.	N, %
2,5-Dimethylpyrrole	No	No	Light yellow, clear	Orange, turbid	10.5	40	8.6
	Yes	No	Yellow tinted, clear	Orange, turbid	10	26	10.3
	No	Yes	Yellow tinted, clear	Light orange, turbid	11	9.6	...
	Yes	Yes	Orange red sediment[d]	Orange, turbid	9.5	540	10.9[e]
2,4-Dimethyl-3-ethyl-pyrrole (kryptopyrrole)	No	No	Yellow tinted, clear	Dark brown	3	1.2	...
	Yes	No	Yellow tinted, clear	Dark brown	3	3.2	...
	Yes	Yes	Dark red, clear	Intense red	0	3.6	...

[a] Alkylated pyrroles were distilled in nitrogen atmosphere immediately before use. [b] Mixtures were slightly yellow to start with, but higher than 25 in Robinson scale. [c] All sediments were rusty colored. [d] Solution was orange colored and turbid after 1 hour. (At that time, other solutions with 2,5-dimethylpyrrole still showed no visible change.) [e] Other analytical data: C, 70.17; H, 7.17; S, 6.70; O calcd. by difference 15.96.

More color loss was observed in the solutions containing *tert*-dodecyl mercaptan, but the amount of sediment formed is much less than that observed for aromatic mercaptans in a similar mixture (Table VI). The indene-*tert*-mercaptan solution, however, produced more sediment with a higher nitrogen content than indene-*n*-mercaptan solution. None of the solutions were acidic. The mechanism of sediment formation in these solutions is not understood. However, the attack of hydroperoxides, formed from the olefins, on the mercaptan and pyrrole is probably an important factor.

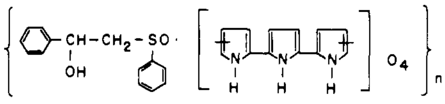
The apparent interactions in hydrocarbons containing aromatic mercaptan-olefin-pyrrole which result in instability are mainly due to the attack of hydroperoxides produced from the thiol-olefin co-oxidation on pyrrole as is shown in the following scheme:


(5)

Because of the great instability of the hydroperoxides at the temperature of the test and the complexity of the system used, other reactions are also probable.

One possibility, that the hydroxysulfoxide rearrangement products of mercaptoethyl hydroperoxide may react with pyrroles, was examined in xylene solutions because these hydroxysulfoxides are not soluble enough in cetane. Dilute xylene solutions of hydroxysulfoxides obtained from mercaptan olefin co-oxidation (*20*) and pyrrole were tested for stability. The data in Table IX show that the pyrrole and hydroxysulfoxide compounds reacted to form black sediment. A very small quantity of black sediment was also produced in the solution of pyrrole alone. The solution of 2-(1-hydroxy)-indanyl *p*-tolyl sulfoxide without pyrrole precipitated some white crystalline sediment. This was found by infrared analysis to be very similar to the original compound, except for a carbonyl peak in the sediment which was absent in the sulfoxide to start with. None of these solutions showed any acidity, which suggested that sulfonic acids were not formed.

An elemental analysis of the black sediment produced from the reaction between pyrrole and (2-hydroxy-2-phenyl)-ethyl phenyl sulfoxide (Table VIII) is shown below, compared with calculated values for a possible pyrrole polymer.


; $C_{26}H_{23}O_6SN_3$ (6)

	Found	Calcd. for $C_{26}H_{23}O_6SN_3$
Carbon	60.48	61.77
Hydrogen	4.88	4.58
Sulfur	6.25	6.34
Nitrogen	8.30	8.31
Oxygen (by difference)	20.09	19.00

The reaction was also studied at 110° F. Some simple sulfides, sulfoxides, and sulfones from the addition of *p*-toluenethiol to indene and the oxidation of the sulfide formed (*19*) were also included in this series of experiments. The data in Table X show that both the hydroxy-substituted and the simple sulfoxide and sulfide produced more color and sediment in the presence of pyrrole. However, there was no change in the presence of a sulfone.

The reaction of an alkylated pyrrole, 2,5-dimethylpyrrole, with sulfur compounds at 210° F. was also examined. The color and sediment values obtained after 16 hours are shown in Table XI. The results indicate a definite reaction between the sulfoxide compounds and pyrrole, forming colored sediment with high nitrogen and sulfur content. The absence of any acidity in the filtrates indicates that sulfonic acid formation probably was not involved in the sediment formation.

Table VIII. Effect of Aliphatic Mercaptan-Olefin-Pyrrole Mixtures[a]

(Storage at 110° F.)

Olefin		Dodecane-thiol	Pyrrole	Period, Days	Color, Rob.	Sediment		
	Mole/l.					Mg./100 ml.	S, %	N, %
1-Octadecene	0.6	Normal	No	28	25	0	...	...
	0.6		Yes	28	2	11	...	...
	0.6	Tertiary	No	28	1	7.8	3.8	...
	0.6		Yes	28	0.5	11.5	1.1	...
Indene	0.3	Normal	No	5	23.5	0.9	...	...
	0.3		Yes	5	19.5	5.6	8.9	1
	0.3	Tertiary	No	5	13.5	8.6	3.8	...
	0.3		Yes	5	10	74.3	3.8	8.8

[a] In cetane solutions containing 0.3 mole/l. each of pyrrole and dodecanethiol.

Table IX. Effect of Pyrrole and Hydroxysulfoxides on Stability of Pyrrole Solutions

(16 hours' storage in xylene solutions at 210° F.)

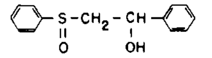
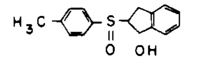
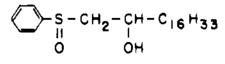
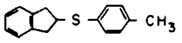
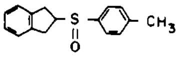
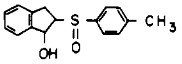
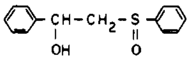
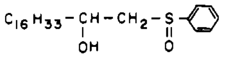
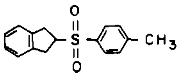
Added Compd., 0.003 Mole/L.			Color, Rob.	Sediment		
Hydroxysulfoxide	M.p., ° C.	Pyrrole		Appearance	Mg./100 ml.	N, %
Nil	...	Yes	25	Black powder	1.5	...
	92–105	No	>25	...	0	...
		Yes	8	Black powder	8	8.3
	136–139	No	24	Almost white crystals	18	...
		Yes	0.3	Black powder	34	5.8
	61–62	No	>25	...	0	...
		Yes	8	Black powder	5.5	4.0

Table X. Effect of Sulfides, Sulfoxides, and Sulfones on Stability of Pyrrole Solutions

(30 days' storage in xylene solutions at 110° F.)

Added Compd., 0.003 Mole/L.			Color		
Sulfur Compd.	M.p., ° C.	Pyrrole	Appearance	Rob.	Sediment, Mg./100 Ml.
Nil	...	Yes	Yellow tint	24	0
	86-86.5	No	Reddish brown	5	0
		Yes	Green	9	3.2
	107-108	No	Medium brown	14	1.0
		Yes	Dark brown	0.5	2.6
	136-139	Yes	Dark green	2.5	4.3
	92-105	No	Yellow	22.5	0
		Yes	Brown	5	1
	61-62	No	Dark yellow	17.5	0
		Yes	Brown	10	0.6
	134.5-135.5	No	Yellow brown	15	0
		Yes	Yellow tint	24	0

In a series of experiments the effect of pyrrole and thiophenol-1-octadecene co-oxidation products on color and sediment formation in cetane was studied (Table XII). In the absence of pyrrole, neither thiophenol and octadecene nor the co-oxidation product, 1-(2-hydroxy)-octadecyl phenyl sulfoxide, caused any color or sediment formation in this solvent at 0.03 mole per liter concentration. In the presence of 0.09 mole per liter pyrrole, however, color and sediment were formed. The pyrrole-thiophenol-1-octadecene system formed more sediment, probably because of the attack of pyrrole by the hydroperoxide intermediate of the co-oxidation reaction.

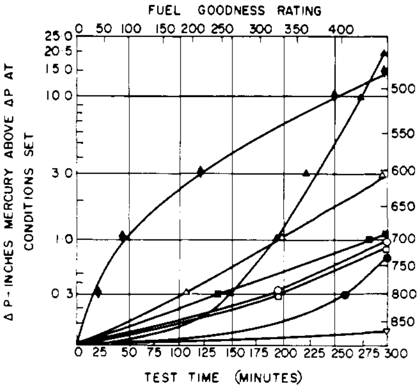
CONDENSATION OF PYRROLES WITH CARBONYL COMPOUNDS

Peroxides can decompose to aldehydes and ketones. Phenols may give quinonic compounds on oxidation. The reaction of such carbonyl compounds with pyrrole is known (*4, 7, 12, 25*). In fuels, the reaction of secondary products of autoxidation may also take part in color- and sediment-forming reactions involving pyrrole. For example, formaldehyde, propionic aldehyde, benzaldehyde, and furfural condensed with pyrrole at room temperature without any added catalyst. The products of such condensations are resinous, colored solids insoluble in saturated aliphatic hydrocarbons. Condensations with indole (replacing pyrrole) also gave colored compounds more soluble in organic solvents.

INSTABILITY OF PETROLEUM FRACTIONS CONTAINING PYRROLE

Previous publications by many authors have shown that both pyrrole-type compounds and mercaptans contribute to the storage instability of petroleum distillates and that

Figure 3. Interaction of *n*-dodecyl mercaptan, 1-octadecene, and pyrrole at high temperature →



Preheater temperature 300° F., filter temperature 400° F.

Legend

Added Compd. in JP-4 (Mole/L.)

	n-Dodecyl mercaptan	1-Octadecene	Pyrrole
▽	...	...	...
□	0.0002	...	...
△	...	0.0002	...
○	...	...	0.0002
■	0.0001	0.0001	...
●	0.0001	...	0.0001
▲	...	0.0001	0.0001
◆	0.0001	0.0001	0.0001

Table XI. Effect of 2,5-Dimethylpyrrole and Sulfoxides on Color and Sediment Formation

(16 hours' storage in xylene solution at 210° F.)

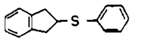
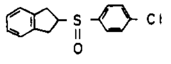
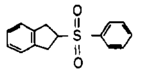
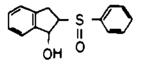
Added Compd., 0.003 Mole/L.				Sediment			
Sulfur Compd.	M.p., ° C.	2,5-Dimethylpyrrole	Color	Color	Mg. per 100 ml.	N, %	S, %
...	...	Yes	16.5 Rob.,	Brown	4.1	...	...
	46-47	No	+1 Say.	...	0	...	...
		Yes	16.5 Rob.,	Dark brown	4.1	...	...
	97-98	No	14.5 Rob.	...	0	...	...
		Yes	10 Rob.,	Brown	18.7	4.2	...
	107-108	No	+16 Say.	...	0	...	...
		Yes	16.5 Rob.	...	3.6	...	...
	148-150	No	15.5 Rob.	...	0	...	...
		Yes	11.5 Rob.,	Black	35.4	4.9	5.19

Table XII. Effect of Pyrrole and Thiophenol–1-Octadecene Co-oxidation Products on Color and Sediment Formation

(3 weeks' storage in cetane solution at 110° F.)

Added Compd., 0.03 Mole/L.	Pyrrole 0.09 Mole/L.	Color		Sediment Mg./100 Ml.
		Appearance	Rob.	
Nil	Yes	Colorless,	> 25	[a]
Thiophenol	Yes	Colorless,	> 25	[a]
Thiophenol Octadecene	No	Colorless,	> 25	[a]
Thiophenol Octadecene	Yes	Yellow-brown,	17	4
Isomer[b]	No	Violet-brown,	19	[a]
Isomer[b]	Yes	Violet-brown,	19	2

[a] No visual sediment.
[b] 1-(2-Hydroxy)-octadecyl phenyl sulfoxide with m.p. 51-2° C.

the organic sediments formed contain a high percentage of both sulfur and nitrogen. Our results may help to explain these observations.

Co-oxidation reactions may also be important in the high temperature instability of petroleum distillates. Therefore, the effect of added *n*-dodecyl mercaptan, 1-octadecene and pyrrole, alone and together, were examined on a JP-4 jet fuel in the CFR fuel coker (*2*). The results (Figure 3) show that when all three sediment precursors were present fuel goodness rating decreased. Similar results were obtained on studying the combinations of thiophenol, 1-octadecene, and pyrrole. In these experiments, the combinations containing both thiophenol and pyrrole produced preheater deposits.

CONCLUSIONS

The instability of petroleum fractions containing sulfur and pyrrolic compounds is the result of complicated interactions between various reactive fuel components. Generally, the contributing effects of pyrrole derivatives and also of the sulfur compounds and pyrroles, in oil deterioration, can be considered as increasing the rate of radical formation (chain initiation), thus promoting oxidation and giving colored and/or insoluble oxidation products.

In this work, a number of reactions have been found to contribute to the instability of synthetic hydrocarbon solutions containing pyrroles, indoles, and their alkyl derivatives. In these reactions, the formation of radicals and oxidation products are interconnected. Pyrroles and mercaptans give rise to radicals on hydrogen abstraction. The radicals, in turn, participate in reactions forming peroxides and yielding deposits of high nitrogen and sulfur content. These reactions are summarized in Figure 4. The attack of pyrroles by hydroperoxides is probably the most important among these reactions. Hydroperoxides containing sulfur are formed at very fast rates in hydrocarbons containing aromatic mercaptans and reactive olefins when in contact with air. By the reaction of these hydroperoxides with pyrroles, pyrrole black-type deposits are formed. These and similar reactions may explain additional decreases of stability on blending different fuel components. They are partially responsible for the known instability of petroleum distillates containing mercaptans, olefins, and pyrroles. From the standpoint of fuel quality, it is important to keep the number of color and sediment precursor types and their absolute amounts at minimum.

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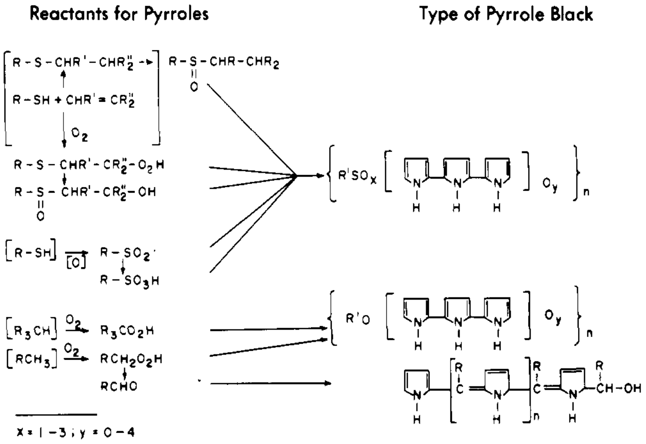

Figure 4. Tentative reactions forming pyrrole black deposits in petroleum

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