is that lesser quantities are required. In general, satisfactory emulsions can be made using only 70% as much free lignin as the sodium salt. The chief disadvantage is an extra step required, since the free lignin would have to be prepared as a separate solution or else added to the water phase before the resin acid.

Another advantage of using the sodium salt of lignin that was not brought out in the present work, but which is a very real asset, is that it can be added as a solution to the finished emulsion to bring it within specifications. The best way to add it is with the emulsifying solution. However, sometimes an emulsion is slightly off specifications, as in the cement test, and it is very helpful to be able to add a stabilizer solution to correct this deficiency without going to the trouble of putting the emulsion through the machine again.

ACTION OF PINE WOOD LIGNIN AS A STABILIZER

Pine wood lignin appears to have a dual role in stabilization of slow-break asphalt emulsions. Its most important function is prevention of the reaction of emulsifying soap with calcium which would cause precipitation and deactivation of the emulsifier. In this respect the lignin acts as a sequestering agent by reacting preferentially with the calcium. For this purpose lignin is preferred over the inorganic sequestering agents because it adds less ash to the system and also because of its better compatibility.

To demonstrate this property more fully kerosene-in-water emulsions were made up in the manner described for asphalt-inwater emulsion and stability toward calcium chloride was observed. Two hundred grams of 25% kerosene-in-water emulsions were made, using 3 grams of resin acid soap as the emulsifier. When put through the colloid mill this emulsion was stable for 2 hours. This procedure was repeated except that 2 grams of hours. anhydrous calcium chloride were added to the water prior to adding to the colloid mill. The resulting emulsion broke after standing for 1 minute. The run was repeated but 1.65 grams of alkali lignin were added in addition to the 2 grams of calcium chloride to the water just before passing through the colloid mill.

The resulting emulsion in this case was stable for 1 hour before beginning to break.

The dispersing action of alkali lignin has been reported in other fields, where it is shown to be effective for clays (2) and carbon black (1). Advantages over organic stabilizers which have been used are better compatibility, generally greater economy, and stability on storage for long periods.

CONCLUSIONS

Alkali lignin, through its sequestering and dispersing properties, is a very effective stabilizer for slow-break asphalt emulsions. The present work shows that satisfactory slow-break emulsions can be prepared using petroleum asphalts that come from a wide variety of crudes. No correlation could be shown between crude source, asphalt properties, or refining variables and ease of emulsification. Pine wood lignin, because of its low price, ready availability, stability on storage, compatibility with all types of asphalt encountered and all common soap emulsifiers, presents an effective answer to one of the emulsion producers most difficult problems.

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Sulfur Compounds as Antioxidants

EFFECT OF SOME STRUCTURAL VARIATIONS ON POTENCY

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N A recent paper (14) β -alkylmercapto ketones were shown to be effective antioxidants using lard as a convenient substrate. Materials of this type have shown antioxidant properties in substrates as diverse as gasoline, styrene, and paraffin wax. Some of the features that affect the potency of these compounds were pointed out and a tentative theory to explain the lower potency of certain materials was suggested. The results of synthesis and testing of additional compounds to provide a better understanding of the problem are described in this paper.

The reaction of the bifunctional sulfur compounds, hydrogen sulfide or ethanedithiol, with α,β -unsaturated ketones leads to ketones having a sulfur attached to the β -carbon atom (3, 15).

 $2CH_3COCH = CH_2 + H_2S \longrightarrow (CH_3COCH_2CH_2)_2S$

 $2CH_{3}COCH = CH_{2} + HSC_{2}H_{4}SH \longrightarrow (CH_{3}COCH_{2}CH_{2}SCH_{2} -)^{2}$

Both these reactions proceed readily in the presence of basic catalysts. Results of testing some of these materials as antioxidants are shown in Table I.

As would be predicted from the results with the β -alkylmercapto ketones, these compounds are potent antioxidants.

One other class of compounds that reacts like the α,β -unsaturated ketones is the α -vinylpyridines. α -Vinylpyridine reacts readily with compounds containing an SH group and materials prepared from it were tested as antioxidants. By proper control of the order of addition and ratio of reactants it was possible to obtain the mercaptan or the sulfide from reaction with hydrogen sulfide (Table II).



The low potency of these materials places them in the same

class as the mercapto nitro and cyano compounds previously reported (14).

In certain cases when an acid catalyst is used to effect condensation, three molecules of mercaptan react with α,β -unsaturated carbonyl compounds by addition across the double bond and formation of the dithioacetal accompanied by elimination of water (12). Data on two such compounds are shown in Table III.

All the compounds examined heretofore have the sulfur attached to the carbon atom β - to the keto or mercaptal group and it was of interest to see whether potent inhibitors could be obtained with sulfur attached to the carbon atom α -, γ -, or δ - to the functional group. Synthesis of compounds with sulfur attached to the α -carbon atom proceeds readily through reaction of the α -chloroketone with the appropriate alkali mercaptide. The γ and δ compounds were prepared by reaction of the chlorosulfides with acetoacetic ester as shown below:

$$\begin{aligned} \text{ClCH}_2\text{CH}_2\text{Cl} + \text{NaSC}_2\text{H}_5 &\longrightarrow \text{ClCH}_2\text{CH}_2\text{SC}_2\text{H}_5 + \text{NaCl} \\ \text{ClCH}_2\text{CH}_2\text{SC}_2\text{H}_5 &+ (\text{CH}_3\text{COCHCO}_2\text{C}_2\text{H}_5)^{-}\text{Na}^+ &\longrightarrow \\ & \text{CO}_2\text{C}_2\text{H}_5 \\ & \text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{CH} &+ \text{NaCl} \\ & \text{COCH}_4 \\ & \text{COCH}_4 \end{aligned}$$

 $C_{2}H_{5}SCH_{2}CH_{2}CH_{2}CH \longrightarrow C_{2}H_{5}SCH_{2}CH_{2}CH_{2}COCH_{3} + C_{2}H_{5}OH + CO_{2}$

Data on these compounds along with those for the corresponding β materials are shown in Table IV.

Only the compounds having sulfur on the carbon atom β - to the carbonyl show any appreciable potency.

It has been suggested (14) that a special steric configuration is necessary for high potency. If, on the other hand, some special chemical property is responsible for high potency, it should be of interest to investigate vinylogs (β) of the β compounds as antioxidants. Synthesis of such a compound was attempted by the following reactions:

$$\begin{array}{c} CH_2 = CH - CH = CHCN + C_2H_5SH \longrightarrow C_2H_5SCH_2CH = \\ CHCH_2CN \\ C_2H_5SCH_2CH = CHCH_2CN + RMgX \longrightarrow C_2H_5SCH_2CH = \\ \downarrow \\ CHCH_2COCH_2 \\ C_2H_5SCH_2CH = CHCH_2CO_2H \end{array}$$

Unfortunately, the last step involving reaction with a Grignard reagent caused decomposition and evolution of a sulfur-containing material. However, it was possible to hydrolyze the nitrile to the acid (4) and to compare this product with β -ethylmercaptopropionic acid (7).

Reaction of a mercaptan with the appropriate acetylenic ketone leads to a β -mercaptovinyl ketone which has the double bond in the α,β position. Such a ketone, which should differ in properties from its saturated analog, was prepared from benzoylacetylene.

Previous datum (14) predicts that the nitrile would be of low potency, but the low potency of the unsaturated acid indicates the necessity of having the sulfur on the β -carbon atom. Comparison of β -ethylmercaptovinyl phenyl ketone with its saturated analog shows a difference in antioxidant properties (Table V).

Compounds that have sulfur attached to the carbon atom β - to the carbonyl in which the carbonyl and/or sulfur are in a ring should have steric relationships very different from those of straight-chain compounds. Two cyclic compounds of this type are shown in Table VI.

The 4-thiacyclohexanone is a material of lower potency as expected, but the ethylmercaptocyclohexanone is better than expected, as the sulfur and oxygen do not have the same steric relationship as in straight-chain compounds.

AOM Time (9), Hours, 0.02% by

tions	nıp	as	ın	straig	ht-e	hain	comp	ound
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DISCUSSION

Several different lards were used in these tests. This was necessary because the data were accumulated over a considerable period of time and the original supply of lard was exhausted. Even though different lards were used, the differences in AOM times are sufficiently great to support the conclusions presented in this paper.

Present-day theory postulates that antioxidants function by reaction of the free radical intermediates with active hydrogen of the inhibitor to break the chain in a fashion similar to that of the following equation:

$ROO. + Inh: H \longrightarrow Inh. + ROO: H$

The free radical Inh. does not have sufficient energy to continue the chain. Unlike the more common types of antioxidants, phenolic or aminoaromatic, no active hydrogen is apparent in the formulas of these sulfur inhibitors. Assuming that the chain is broken at the same point by the sulfur inhibitors, two methods by which this can occur can be pictured.

1. The sulfur compound may serve as an easily oxidized material to destroy the free radicals by a reaction of the type $2\text{ROO.} + \text{H}_2\text{O} + \text{RSR} \longrightarrow 2\text{ROOH} + \text{RSOR}$. The sulfoxide can

Compound	Formula	° C.	° C. –	Mm,	Weight
5-Thianonane-2,8- dione	CH2COCH2CH2				
	CH3COCH2CH2		100-102	2	60 <i>ª</i>
5,8-Dithiadodecane-2,-	$CH_{3}COCH_{2}CH_{2}SCH_{2}$				
11-dione	CH ₃ COCH ₂ CH ₂ SCH ₂	42-43			94 b
	$C_{6}H_{5}$				
1,3,8,10-Tetraphenyl-	C6H5COCH2CH-SCH2				
4,7-dithiadecane-1,- 10-dione	C6H5COCH2CH-SCH2	173-174	• • • • •		426
	C6H5				
^a In 4.5-hour lard. ^b In 9-hour lard.					
TABLE I	I. Sulfur Compoun	DS FROM	α-VINYLPY	RIDINE	
Compound	Formula B.F	°., ° C.	Pressure, A Mm.	OM Time, E 0.02% by W	Iours, eight
/	\land				

TABLE I. SULFUR COMPOUNDS CONTAINING TWO CARBONYL GROUPS

М.Р.,

В.Р.,

Pressure,

 β -(α -Pyridyl)-ethyl mercap-CH2CH2SH 108-109 20<16a tan -(α-Pyridyl)-ethyl sulfide 185-190 3 $< 17^{\circ}$ Ethyl β-(α-pyri-dyl) ethyl sul-fide CH2CH2SC2H 129 - 13020 10^{a} ^a In 4-hour lard.

TABLE III.	TRIS-(ETHYLMERCAPTO)-ALKANES
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Compound	Formula	B.P., ° C.	Pressure, Mm.	AOM Time, Hours, 0.02% by Weight
1,1,3-Tris-(ethyl- mercapto)-pro- pane	$\mathbf{SC}_{2}\mathbf{H}_{1}$	95-97	2	<20°
1,1,3-Tris-(ethyl- mercapto)-bu- tane	$\mathbf{CH_{9}CHCH_{2}CH(SC_{2}H_{b})_{2}}_{SC_{2}H_{b}}$	90-92	1	<19ª

^a In 4.5-hour lard.

hexanone. But because of the flexibility of the cyclohexanone ring, it is possible to effect fairly close approximation of the sulfur and the oxygen. The β -ethylmercaptovinyl phenyl ketone is of interest, since the formation of an allenic system would be necessary to permit enolization; the high energy of such a system would inhibit its formation.

EXPERIMENTAL

REACTIONS OF HYDROGEN SULFIDE AND ETHANE DITHIOL

Compound	Formula	B.P ° C.	Pressure, Mm.	M.P., °C.	AOM Time, Hours 0.02% by Weight
a-Alkylmercaptoacetophe- none	RSCH ₂ COC ₆ H ₅ ^a	12 4-12 9	4		<21 b
β-Ethylmercaptopropio- phenone	C ₂ H ₅ SCH ₂ CH ₂ COC ₆ H ₅			45	91¢
B-Alkylmercaptoethyl methyl ketone	RSCH2CH2COCH3ª	91-94	16		386
γ-Ethylmercaptopropyl methyl ketone	C ₂ H ₅ SCH ₂ CH ₂ CH ₂ COCH ₇	107-110	20	.	<16°
Ethyl α-(3-thiapentyl)-ace- toacetate	CoCH: C2H4SCH2CH2CH				
	CO ₂ C ₂ H ₅	115	3		<16¢
m., 1 ((1) (1) 1)	COCH:	· ·			
Ethyl α -(4-thianexyl)-ace- toacetate	C2H6SCH2CH2CH2CH	122 - 128	2		<160
	CO ₂ C ₂ H	5			

react further to form the sulfone. This mechanism implies that the β -carbonyl is an activating group which causes the sulfur to be more easily oxidized, since alkyl sulfides and sulfoxides are impotent antioxidants; also oxidation of a β -alkylmercapto ketone to the sulfone destroys its potency (14). It offers no explanation for the unexpected variations in potency that have been suggested previously as due to steric relationships.

2. An available hydrogen can be produced by an enolization of the keto group. The enol should be capable of stabilization by chelation with the sulfur on the β -carbon atom.

WITH α,β -UNSATURATED KE-TONES. One mole of the sulfur compound reacts readily with 2 moles of α,β -unsaturated ketone in the presence of a few drops of piperidine.

REACTIONS OF α -VINYLPYRI-DINE WITH THIOL COM-POUNDS. No catalyst is necessary for the reaction of α -vinylpyridine, but a few drops of piperidine speed it up.

FORMATION OF THE TRISAL-KYLTHIO ALKENES FROM MERCAPTANS AND α,β -UN-SATURATED ALDEHYDES. The α,β -unsaturated aldehydes react very vigorously with mercaptans in the presence of anhydrous hydrogen chloride.

 α -ALKYLMERCAPTOACETOPHENONE. A solution of sodium mercaptide in methanol was heated under reflux with an equimolar quantity of α -chloroacetophenone.

 α -ETHYLMERCAPTOPROPIOPHENONE. Vinyl phenyl ketone (10) reacted readily with ethanethiol in the presence of a trace of piperidine.

 α - and δ -ALKYLMERCAPTO KETONES. An excess of ethylene chloride (5 moles) or 1,3-dichloropropane was boiled under reflux with a methanolic solution of sodium ethyl mercaptide (1 mole).

TABLE V. UNSATURATED ALKYLMERCAPTO CARBONYL COMPOUNDS

0		R	Compound	Formula	M.P., ° C.	B.P., ° C.	Pressure, Mm.	AOM Time, Hours
RSC CC $-R' \rightarrow \leftarrow$			β-Ethylmercaptopropionic acid	C ₂ H _b SCH ₂ CH ₂ CO ₂ H		140-142	21	56 *
Ţ	TT		6-Thia-3-octenoic acid 6-Thia-3-octenoic nitrile	$C_2H_6SCH_2CH = CHCH_2CO_2H$ $C_2H_6SCH_2CH = CHCH_2CN$	46-47	104-107	1.5	135
1		<u>с</u> —б	B-Ethylmercaptovinyl phenyl ketone	$C_2H_5SCH = CHCOC_6H_5$		125-130	0.2	17 °
		R'	^a 0.02% by weight in 5-h b 0.02% by weight in 9-h c 0.20% by weight in 5-h	our lard. our lard. our lard.				

If an intermediate such as II is responsible for the antioxidant activity of the sulfur compounds, it explains why the compounds capable of assuming this configuration only with considerable strain belong to the class of the less effective inhibitors. The less effective inhibitors include the sulfur compounds derived from *tert*-alkyl or aryl mercaptans: 3-keto-tetrahydrothiophene, 2,5-bis-(1ethylmercaptobenzyl)-cyclopentanone, β -ethylmercaptovinyl phenyl ketone, 3-ethylmercaptocyclohexanone, and 3,3,5,5-tetramethyl-4-thiacyclohexanone. α -, γ -, and δ -Alkylmercapto ketones or acids are in a separate category and are consistently poor inhibitors. Of these materials all may be classified as being inhibitors of low potency, except for the 3-ethylmercaptocyclo-



The solutions were distilled first at atmospheric and then at reduced pressure. β -Ethylmercaptoethyl chloride boils at 55–58°/ 22 and γ -ethylmercaptopropyl chloride at 69-73°/20. The chlorides (0.5 mole) were added to a solution of sodio ethyl acetoacetate (0.5 mole) in absolute ethanol. Hydrolysis to the ketone was effected by stirring with 5% sodium hydroxide at room temperature.

6-THIA-3-OCTENOIC ACID. Ethanethiol (1 mole) added readily to "cyanobutadiene (13) in the presence of piperidine (5). Hydrolysis to the free acid was carried out according to Coffman (4).

B-ETHYLMERCAPTOVINYL PHENYL KETONE. Ethanethiol (1 mole) added readily to benzoylacetylene (1 mole) (2, 8) in the presence of piperidine.

3-ETHYLMERCAPTOCYCLOHEXANONE. Ethanethiol added readily to cyclohexenone (1) in the presence of piperidine.

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Ethyl Maleopimaric Soap as Emulsifier for GR-S Polymerizations

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HE internal conjugated double bonds in abietic-type acids, which appear to inhibit addition polymerization, have been modified in a commercial emulsifier by disproportionation of rosin to yield a mixture consisting essentially of hydro- and dehydroabietic acids (12). Another approach, adopted by the Southern Regional Research Laboratory in an effort to develop pine gum derivatives suitable for commercial exploitation, is elimination of the conjugation by a Diels-Alder reaction with



Disodium Soap of Maleic Anhydride Addition Product of Ethyl Levopimarate (Ethyl Maleopimaric Soap)

maleic anhydride (14). A derivative of this type was evaluated as an emulsifier for the polymerization of GR-S at 122° F., but the reaction rates were lower than desired (8). The use of the better quality maleopimaric acid obtained by the process described by Waite, Collins, and Summers (16) for the preparation of the ethyl maleopimaric soap yielded a product that appeared to be satisfactory. The results obtained with a sample of the improved product, which has the nominal formula presented herewith, are reported.

PROCEDURE

Butadiene-styrene copolymers were prepared in 5-gallon reactors lined with glass or stainless steel and equipped with 3-inch diameter marine-type impellers rotated at 1125 r.p.m. The charges were prepared according to the following formula and then polymerized at 122° F. (50 $^{\circ}$ C.):

Ingredient	Parts by Weight
Butadiene Styrene DDM (oommercial n-dodecyl mercaptan) Ethyl maleopimaric soap or Dresinate 731° Potassium persulfate Water	$71.5^{a} \\ 28.5^{a} \\ 6 \\ 4.3 \\ 0.30 \\ 180$
a Duna Iraala	

^a Pure basis. ^b Varied to obtain copolymers with a Mooney viscosity of 50 ML-4 at $72\pm 3\%$ hydrocarbon conversion. ^c Dresinate 731 is a registered trade-mark for the sodium soap of dispro-portionated rosin acid as manufactured by the Hercules Powder Co.

The pH of the soap solutions was adjusted to $10.2\,\pm\,0.2$ with sodium hydroxide. The extent of polymerization was calculated from the total solids contents of samples of vented latex removed from the reactor during the course of polymerization. The polymerizations were stopped at $72 \pm 3\%$ conversion by adding