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SYNTHETIC LUBRICANTS

William E. Garwood, Haddonfield, John W. Brooks, Wenonah, and Alexander N. Sachanen, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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This invention has to do with the condensation of normal, alpha mono-olefins, conjugated olefinic compounds and mercaptans or thiols.

As is well known to those familiar with the art, olefins have previously been polymerized; so also have vinyl aromatic hydrocarbons. Olefins and vinyl aromatic hydrocarbons have also been reacted together. In the latter instance, however, copolymerization is generally incomplete. For example, when decene-1 and styrene are copolymerized at 600° F., an oil containing a polystyrene cloud at room temperature (20–25° C.) is formed. The oil thus obtained possesses approximately the same oxidation stability as uninhibited Pennsylvania SAE 10W mineral oils. Vinyl aromatic hydrocarbons, such as styrene, when reacted with mercaptans form products characterized by very low viscosity indices. In effect, then, when any two of the foregoing reactants—olefins, vinyl aromatic hydrocarbons, and mercaptans—are reacted together, the yield of viscous oil is either insufficient or the viscous oil suffers from one or more shortcomings, such as cloud formation, relatively low oxidation stability or low viscosity index (V. I.).

It has now been discovered that certain normal, alpha mono-olefins condense with conjugated olefinic hydrocarbons and thiols, under conditions hereinafter defined, with the formation of highly desirable viscous oils. These oils have molecular weights less than about 1000, generally within the range of 400 to 600. The oils so formed are free from the shortcomings of olefin-vinyl aromatic hydrocarbon copolymers, as illustrated by the 1-decene-styrene copolymer referred to above. Further, the viscous oils of this invention are unusually stable. Catalytic oxidation stability tests demonstrate them to be superior to condensation products of decene-1 alone, to condensation products of decene-1 and styrene, and to uninhibited Pennsylvania type mineral oils. The characteristics of the new oils are such as to make them outstanding synthetic lubricants, for use alone or blended with other lubricants.

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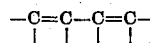
Reactants

The mono-olefin reactants of this invention are normal or straight-chain alpha compounds, and contain from five to eighteen carbon atoms per molecule. Such mono-olefins are normally liquid at temperatures of the order of 20–25° C. Illustrative of such mono-olefins are the following: pentene-1, octene-1, decene-1, dodecene-1, octadecene-1 and the like. Preferred of such olefins, however, are those having from eight to twelve carbon atoms per molecule, with decene-1 representing a particularly desirable olefin. It will be clear from the foregoing examples that an alpha olefin may also be referred to as a 1-olefin.

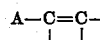
Not only may the mono-olefins of the aforesaid character be used individually in this invention, but they may also be used in admixture with each other. In addition, olefin mixtures containing a substantial proportion of such mono-olefins may be used. Preferred of such mixtures are those containing a major proportion of a 1-olefin or of 1-olefins. Representative of such mixtures are those obtained by the cracking of paraffin waxes and other paraffin products; those obtained from the Fischer-Tropsch and related processes.

These hydrocarbon mixtures may contain, in addition to the 1-olefin or 1-olefins, such materials as: other olefins, paraffins, naphthenes and aromatics.

Olefinic compounds contemplated herein for condensation with normal, alpha mono-olefins and thiols are of conjugated character and include aliphatic compounds and alkenyl-substituted aromatic compounds. Conjugated olefins are characterized by the grouping



and conjugated alkenyl-substituted aromatic compounds are characterized by



wherein A is an aromatic nucleus, an unsaturated

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group of which is in conjugated relationship with the alkenyl group.



The conjugated paraffinic hydrocarbons and derivatives thereof are represented by: butadiene, isoprene (2-methyl butadiene), cyclopentadiene, methyl isoprene; halogen-substituted materials such as chloroprene (2-chloro-butadiene) and 1-bromo butadiene; and the like. Butadiene provides outstanding synthetic oils and is particularly preferred.

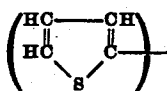
The conjugated alkenyl-substituted aromatic hydrocarbons, and their derivatives, may be mono- or poly-nuclear in character. Of the mono-nuclear or benzene series, styrene or vinyl benzene is a typical and preferred example. Vinyl-diphenyl is another illustrative mono-nuclear compound. Representative ankenyl-substituted poly-nuclear hydrocarbons are vinyl naphthalene, vinyl anthracene, etc. Derivatives of such hydrocarbons are also contemplated herein and include halogen-substituted materials such as p-chlorostyrene, alkoxy-substituted materials such as p-methoxy styrene, and the like.

As will be noted from the character of the foregoing typical substituted, conjugated olefinic hydrocarbons, substituent groups which may be present are those which do not interfere with the condensation of the conjugated olefinic compound with the aforesaid alpha mono-olefin and thiol. In other words, a substituent group which may be present in the conjugated olefinic hydrocarbon is one which is substantially inert or unreactive in the condensation. The substituent group, however, generally modifies the character of the oil product, yet in all cases, the products are characterized by unusual stability and are useful as lubricants. By way of illustration, when p-chloro-styrene is used, the synthetic lubricant formed possesses extreme pressure properties. Similarly, a fluoro-substituted styrene imparts additional stability to the synthetic lubricant product as well as extreme pressure properties.

It will be understood, of course, that mixtures of the aforesaid conjugated olefinic hydrocarbons, and their aforesaid derivatives, may be used in place of the individual reactant. Similarly, mixtures containing substantially, preferably major, proportions of one or more of said conjugated olefinic compounds may be used. An example of such a mixture is a crude styrene containing ethylbenzene.

Preferred of the alkenyl-substituted aromatic compounds, in view of the outstanding character of the products obtained therewith is styrene.

As indicated above, mercaptans or thiols are condensed herein with the aforesaid normal, alpha mono-olefins and conjugated olefinic compounds, and such compounds may be represented by the general formula RSH, wherein R may be hydrogen; a hydrocarbon group such as alkyl, alkaryl, aryl, or aralkyl; or a heterocyclic group such as thienyl (for example)



Typical of such compounds are hydrogen sulfide; alkyl thiols-methyl, ethyl, propyl, n-butyl, secondary-butyl, tertiary-butyl, hexyl, octyl, dodecyl, etc., thiols; alkaryl thiols-methyl thio-phenol, t-butyl thiophenol, t-butyl thionaphthol; aryl thiols-thiophenol, α -thionaphthol, β -thionaph-

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thol; aralkyl thiols-benzyl thiol, phenyl ethylthiol; heterocyclic thiols-thiophenethiol, furan-thiol. Thiophenethiol is described, together with methods for its preparation, in copending application Serial No. 721,454, filed January 10, 1947. Polythiols are also contemplated herein; however, such materials are generally used in smaller quantities than the monothiols.

Of the thiols represented by the general formula, those containing a hydrocarbon or heterocyclic group are preferred. Of the latter compounds, n-butyl mercaptan, thiophenol and thiophenethiol are particularly preferred inasmuch as synthetic lubricants obtained therewith are of outstanding character.

Reaction conditions

Condensation of the aforesaid reactants is affected at elevated temperatures. It appears that temperatures as low as 400° F. and as high as 900° F. can be used in some instances, however, temperatures of the order of about 500° F. to about 800° F. are most satisfactory. The preferred temperature range, as shown hereinbelow, is from about 600° F. to about 750° F.

Condensation is generally complete in from one to twenty hours, preferably from three to ten hours, with the higher reaction temperatures being used for the shorter reaction periods and with the lower reaction temperatures being used for the longer reaction periods.

Pressures ranging from atmospheric to 4000 lbs. per square inch may be used. In general, it is desirable to use sufficient pressure to maintain the reactants in liquid state.

Proportion of reactants can be varied considerably to form products suitable for different uses. With one molar proportion of normal, alpha mono-olefins as the basis, from about 0.01 to about one molar proportion of conjugated olefinic compound, such as a vinyl aromatic compound, and from about 0.001 to about one molar proportion of thiol, provide satisfactory products. Preferred proportions for forming outstanding synthetic lubricants, however, are from about 0.05 to about 0.5 molar proportion of conjugated olefinic compound and from about 0.01 to about 0.5 molar proportion of thiol, with one molar proportion of normal, alpha mono-olefin. By proper proportioning of reactants, synthetic lubricants may be obtained, or blending stocks for use with mineral oils to improve the latter in regard to oxidation stability, viscosity index, and/or pour point properties, may be obtained. Condensation products which are useful as lubricating oil additives or adjuvants in concentrations as low as two per cent in mineral oil to effectively stabilize the latter against oxidation, are formed when a relatively large amount of thiol and conjugated olefinic compounds are used. Products of the latter type however, are characterized by low viscosity indices. As demonstrated hereinbelow in the illustrative examples, optimum conditions for forming the synthetic lubricants may be used, and the resulting synthetic lubricant may be reacted with an additional quantity of a thiol with the same or different thiol to form a product of higher sulfur content and of increased oxidation stability.

It will be understood, of course, that the condensation is aided by providing mixing of the reactants. This may be provided by using various agitating means which are well known in the art. At the reaction conditions, the reactants are readily soluble and homogeneity is easily obtained.

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Examples

In order to illustrate the principles of this invention, the results of a series of typical, and non-limiting, condensations are set forth in tabular form in Table I below. These condensations were carried out in a rocking-type bomb (American Instrument Co.). The reactants were charged to the bomb, which was then heated to the desired temperature for the desired length of time. Thereafter, the bomb was cooled, and discharged. The contents of the bomb were vacuum distilled to remove unreacted materials. It should be noted that the reaction times, recited as "Time, Hours" in Table I, represent the time intervals during which the bomb was maintained at the desired temperature, and do not include the time intervals necessary to heat the bomb and its contents to the desired temperature, and do not include the time intervals necessary to cool the bomb after heat to the bomb has been discontinued. The condensation products discharged from the bomb, or other reaction vessel, were distilled and filtered, as in the runs shown in Table I. To distinguish the condensation products from the distillate fractions thereof, the refined oils are identified as "residual oils." The latter term identifies the oils from which unreacted materials and products of intermediate boiling range have been separated.

All of the tests and analyses to which the residual oils in Table I were subjected are well known standard tests. In this connection, it will

be noted that the designation "N. N." refers to the neutralization number, which is a measure of the acidity of the oil.

Styrene used in these condensations contained a fraction of one per cent of p-tertiary-butyl catechol, the latter acting as a stabilizer or polymerization inhibitor. This styrene material is the commercial product now available.

By way of illustration, the procedure followed in run 1 of Table I below, is provided in detail. A mixture of 336 parts by weight (3 molar proportions) of octene-1, 39 parts by weight (0.375 molar proportion) of styrene and 6 parts by weight (0.067 molar proportion) of n-butyl mercaptan was charged to a stainless steel rocking-type bomb (American Instrument Co.). After the bomb head was secure, approximately 1500 lbs. per square inch of nitrogen was pressured into the bomb to check for leaks. The pressure was then released, the system was again closed and the bomb was heated to 600° F. in the course of 1½ hours and held at that temperature for ten hours. During the reaction, a pressure of 200 lbs. per square inch developed. After cooling the bomb to room temperature, (70° F.), during a period of about three hours, the reaction product was discharged into a flask and topped under reduced pressure (5 mms. Hg) to a liquid temperature of 420° F. and a vapor temperature of 345° F. A quantity, 118 parts by weight, of residual oil was obtained and was filtered through a thin coat of a diatomaceous earth filter aid (Super Filtrol).

Table I

Reference	Reaction Conditions										Temp., ° F.	Time, Hrs.	Max. Press. P. S. I. G.
	Olefin			Styrene		Mercaptan							
	Name	Parts by Weight	Moles	Parts by Weight	Moles	Name	Parts by weight	Moles					
CONDENSATION OF OLEFINS WITH STYRENE AND ALKYL MERCAPTANS													
Run:													
1.....	Octene-1.....	336	3	39	0.375	N-butyl.....	6	0.067	601	10		200	
2.....	Octene-2.....	336	3	39	0.375	do.....	6	0.067	602	10		180	
3.....	2-Ethylhexene-1.....	336	3	39	0.375	do.....	6	0.067	602	10		<200	
4.....	Decene-1.....	420	3	39	0.375	do.....	6	0.067	504	10½		100	
5.....	do.....	420	3	39	0.375	do.....	6	0.067	598	10		<200	
6.....	do.....	420	3	39	0.375	do.....	6	0.067	645	10		700	
7.....	do.....	420	3	39	0.375	do.....	6	0.067	700	3		800	
8.....	do.....	420	3	39	0.375	do.....	6	0.067	750	3		750	
9.....	do.....	420	3	10	0.096	do.....	6	0.037	653	10		200	
10.....	do.....	420	3	39	0.375	T-butyl.....	6	0.067	652	10½		900	
CONDENSATION OF OLEFINS WITH STYRENE AND AROMATIC MERCAPTANS													
Run:													
11.....	Decene-1.....	420	3	39	0.375	Thiophenol.....	6	0.054	601	10½		<100	
12.....	do.....	420	3	39	0.375	do.....	6	0.054	647	10		600	
13.....	do.....	840	6	78	0.75	do.....	6	0.054	654	9½		150	
14.....	Product of Run 13.....	500				do.....	30	0.273	605	5½		<100	
CONDENSATION OF OLEFINS WITH STYRENE AND HETEROCYCLIC MERCAPTANS													
Run:													
15.....	Decene-1.....	420	3	39	0.375	3-Thiophenethiol.....	1	0.008	601	10½		650	
16.....	Product of Run 15.....	220				do.....	9	0.077	600	5		150	
17.....	Decene-1.....	420	3	39	0.375	do.....	20	0.172	599	10		300	
18.....	do.....	420	3	39	0.375	do.....	2	0.017	648	10		450	
19.....	do.....	140	1	104	1	do.....	116	1	605	10		<200	
20.....	do.....	840	6.0	78	0.75	None.....			600	10½		400	
CONDENSATION OF OLEFIN WITH BUTADIENE AND ALKYL MERCAPTAN													
Run 21.....	Decene-1.....	420	3	27	0.5	N-butyl.....	6	0.067	650	11½		620	

See footnotes at end of table.

Table I—Continued

Reference	Residual Oil									
	Parts by Weight	Weight Percent Yield	Cloud Point, ° F.	K. V. @ 100° F., Cs	K. V. @ 210° F., Cs	V. I.	Pour Point, ° F.	N. N.	Specific Gravity	Weight Percent S
CONDENSATION OF OLEFINS WITH STYRENE AND ALKYL MERCAPTANS										
Run:										
1.....	118	31		22.92	4.18	89.6	<-30	0.2	0.8729	0.30
2.....	43	11.3		38.24	4.93	42	<-30	0.1	0.9752	0.91
3.....	20	5.2		35.61	4.39	<0				
4.....	58	12.4		34.45	5.25	88.8	<-30	0.2	0.9117	0.84
5.....	112	24.1	-28	17.11	3.70	116.4	<-30	0.1	0.8560	0.37
6.....	156	33.6		21.11	4.29	126.4	<-30	0.2	0.8550	0.18
7.....	174	37.4		18.86	3.99	125.7	<-20	0.2	0.8545	0.26
8.....	121	28		24.73	4.61	114.5	-5	0.2	0.8644	0.10
9.....	131	30		24.03	4.70	129.3	<-30	0.2	0.8493	0.28
10.....	77	18.6		25.22	4.58	106.4	<-30	0.2	0.8702	1.07

CONDENSATION OF OLEFINS WITH STYRENE AND AROMATIC MERCAPTANS

Run:										
11.....	80	17.2	-28	15.93	3.55	117.0	<-30	0.1	0.8607	0.73
12.....	96	20.6		22.31	4.98	118.1	<-30	0.1	0.8623	0.27
13.....	124	31		23.13	4.48	120.1	<-30	0.1	0.8597	0.10
14.....	172	31.5		28.12	5.03	117.5	-5	0.3	0.8633	0.72

CONDENSATION OF OLEFINS WITH STYRENE AND HETEROCYCLIC MERCAPTANS

Run:										
15.....	85	36	-34	19.07	4.11	136.1	-35	0.2	0.8565	0.25
16.....	83	35		22.11	4.42	126.6	<-30	0.1	0.8718	2.11
17.....	70	14.6		20.96	4.08	104.1	<-30	0.3	0.936	6.38
18.....	165	35.8		23.20	4.60	130	<-30	0.1	0.8555	0.39
19.....	108	30		66.05	6.59	30.3	-35	0.8	1.0679	19.94
20.....	493	53.6	+60	24.0	4.80	137.3	-25	0.1	0.8514	

CONDENSATION OF OLEFIN WITH BUTADIENE AND ALKYL MERCAPTAN

Run 21.....	151	33.4		25.14	5.04	141	-30	Nil	0.8438	0.12
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¹ From 390 g. of reaction product. Remainder used in run 14.
² From 228 g. of reaction product. Remainder used in run 15.
³ Weight of total reaction product from the indicated run.

A comparison of runs 1-3 of Table I, reveals the critical nature of the olefin reactant. As shown by these runs, a normal, alpha mono-olefin, octene-1, reacts to form a substantially greater yield of a superior oil than does either the corresponding 2-olefin and the corresponding branched-chain octene. The oil product obtained by octene-1 has a significantly higher V. I. than the oil products from octene-2 and 2-ethylhexene-1. This is summarized in the following tabulation:

Run No.	Olefin	Residual Oil		
		Yield, Weight Percent	K. V. @ 210° F., Cs	V. I.
1.....	Octene-1.....	31.0	4.18	89.6
2.....	Octene-2.....	11.3	4.93	42
3.....	2-ethylhexene-1.....	5.2	4.39	<0

Runs 4-8 show the influence of reaction temperature and time upon the condensation of decene-1, styrene and n-butyl mercaptan. Temperatures of about 600-750° F. with times of ten

to three hours, are most satisfactory in that oil products of high viscosity index and low pour point are formed in relatively high yield. These salient features are revealed in the following tabulation.

Run No.	Reaction Conditions		Residual Oil			
	Temp., ° F.	Time, Hrs.	Yield, Weight Percent	K. V. @ 210° F., Cs	V. I.	Pour Point, ° F.
4.....	504	10½	12.4	5.26	88.8	<-30
5.....	598	10	24.1	3.70	116.4	<-30
6.....	645	10	33.6	4.29	126.4	<-30
7.....	700	3	37.4	3.99	125.7	<-20
8.....	750	3	26.0	4.61	114.5	-5

A comparison of runs 6 and 9 indicates that as the proportion of styrene is increased the yield of residual oil increases without materially detracting from the character of the oil product. This feature is shown in the following tabulation wherein a blank run is shown for the condensation of decene-1 and n-butyl mercaptan in the absence of styrene; in the blank run, the proportions

of mono-olefin and mercaptan are the same as in runs 6 and 9.

Run No.	Styrene, Molar Propn.	Residual Oil		
		Yield, Weight Percent	K. V. @ 210° F., Cs.	V. I.
Blank.....	0	15.5	4.25	130.1
9.....	0.096	30	4.70	129.3
6.....	0.375	33.6	4.29	126.4

Runs 6 and 10 show the relationship of mercaptan structure with the properties of the oil products. The straight chain structure of n-butyl mercaptan, in contrast to the branched-chain structure of tertiary-butylmercaptan, appears to have a salutary effect upon the yield and V. I. In addition, the oil product obtained from the n-butyl compound has a lower sulfur content. These features are revealed in the following tabulation:

Run No.	Mercaptan	Residual Oil			
		Yield, Weight Percent	K. V. @ 210° F., Cs.	V. I.	S, Weight Percent
6.....	n-Butyl	33.6	4.29	126.4	0.18
10.....	t-Butyl	16.6	4.58	106.4	1.07

Oil products obtained with aromatic mercaptans are shown in runs 11-14. It will be noted that run 14 involves reaction of additional thiophenol with the reaction product of run 13. Additional sulfur is introduced without affecting the characteristic properties of the oil.

A heterocyclic mercaptan, thiophenethiol, is shown in runs 15-19. A further illustration of reacting the olefin, vinyl aromatic and mercaptan under optimum conditions to obtain a residual oil of high yield, high viscosity and high viscosity index, and thereafter increasing the sulfur content with the additional mercaptan, is shown by runs 15 and 16. This procedure is preferred when producing oil blending stocks of relatively high sulfur content, where viscosity index and pour point of the oils blended therewith are improved by virtue of the high viscosity index and low pour point of the synthetic blending stocks. Runs 15, 17 and 19 illustrate the effect of the quantity of thiol used in the condensation. When the molar proportion of thiol is increased such that the olefin:styrene:thiol ratio is 1:1:1, the viscosity index of the oil product falls off considerably, specific gravity increases and the sulfur content is increased greatly. The oil product of run 19, finds utility as a lubricant in operations wherein high viscosity index is not required and also finds utility as an oil addition agent for lubricating oils.

Run 20 is shown herein to demonstrate the difference between an oil product obtained by condensation of a 1-olefin and a vinyl aromatic compound in the absence of a thiol, and an oil product obtained with a thiol. An effective comparison is provided by runs 5, 11, 15 and 20. It will be clear that the oil obtained in run 20, in which no thiol was used, has excellent viscosity index and

pour point properties, but has an undesirably high cloud point, 60° F. In contrast, the oils of runs 5, 11 and 15 have low cloud points. Emphasizing this relationship, the salient features of these runs are tabulated below:

Run No.	Decene-1, Molar Propn.	Styrene, Molar Propn.	Mercaptan		Residual Oil Cloud Pt., °F.
			Name	Molar Propn.	
20.....	6	0.75	None.....	-----	+60
5.....	3	0.375	n-Butyl.....	0.067	-26
11.....	3	0.375	Thiophenol.....	0.054	-28
15.....	3	0.375	3-Thiophenethiol.	0.008	-34

Infrared analysis of the residual oil of run 5 shows the benzene nucleus to be present therein, thus indicating that styrene has reacted into the product even though the polystyrene cloud is not present.

The effect of a thiol upon yield, viscosity index and sulfur content is shown by the following comparison:

Run No.	3-Thiophenethiol Molar Propn.	Residual Oil			
		Yield, Weight Per Cent	K. V. @ 210° F., Cs.	V. I.	S, Weight Per Cent
20.....	0	53.6	4.80	137.3	-----
15.....	0.008	36	4.11	136.1	0.25
17.....	0.172	14.6	4.08	104.1	6.38
19.....	1.0	30	6.59	30.3	19.94

It will be seen that the advantages obtained by the use of thiols are at the expense of yield, but it must be kept in mind that the oil obtained without a thiol is characterized by a poly-styrene cloud and is not usable as such.

Run 21 illustrates an excellent synthetic oil obtained with butadiene as the polyolefinic reactant.

That the residual oils of this invention have excellent stability is shown by results of a catalytic oxidation test, the results being shown below in Table II. This oxidation test reveals the stability of oils toward catalytic oxidation.

The test oil, 25 ccs., is placed in a 200 x 25 mms. test tube with 15.6 square inches of sand-blasted iron wire, 0.78 square inches of polished copper wire, 0.87 square inch of polished aluminum wire, and 0.167 square inch of polished lead plate. Dry air is passed through the sample of oil at a rate of 10 liters per hour. The test tube is heated at 260° F. for 40 hours in an aluminum block bath. The results reported at the end of the test are: neutralization number (N. N.); percent viscosity increase at 210° F.; sludge and lacquer; lead weight loss (in milligrams); and appearance of copper. The oil is compared with a reference oil of similar viscosity and is rated on the basis of viscosity increase, N. N. increase, sludge and lead weight loss. A maximum of 3 demerits is assigned to each factor rated. The sum of the demerits for an oil is called the stability number and ranges from 1 to 12. The reference mineral oils, solvent-refined Pennsylvania oils, have a stability number of 6 to 7.

Table II.—Oxidation stability of oils

Oil	N. N.	K. V. @ 210° F., Cs.	Per Cent Viscosity Increase	Sludge, Tube	Copper Coil	Pb. Loss, Mg.	Stability Number
10W Mineral Oil Base Stock ¹	16	12.91	125	Nil.....			6 or 7
Run 20.....	8.8	9.44	96.2	Nil.....	Dull Copper.....	235 238.8	6
PRODUCTS FROM CONDENSATION OF OLEFINS WITH STYRENE AND ALKYL MERCAPTANS							
Run 6.....	0.8	4.43	3.2	Nil.....	Brown Stain.....	23.9	0
Run 10.....	1.0	4.92	7.4	Nil.....	Gray Stain.....	14.0	0
PRODUCTS FROM CONDENSATION OF OLEFINS WITH STYRENE AND AROMATIC MERCAPTANS							
Run 12.....	12.3	8.23	88.7	Nil.....	Brassy.....	251.3	5
Run 13.....	16.3	9.67	115	Nil.....	Brown Stain.....	243.2	7
Run 14.....	0.3	5.34	6.10	Nil.....	do.....	159	2
PRODUCTS FROM CONDENSATION OF OLEFINS WITH STYRENE AND HETEROCYCLIC MERCAPTANS							
Run 15.....	5.0	4.97	20.9	Nil.....	Brown Stain.....	242.6	3
Run 16.....	0.8	4.62	4.5	Nil.....	Dark Brown.....	36.6	0
Run 17.....	1.1	4.36	6.8	Nil.....	Black Stain.....	36.3	0
Run 18.....	10.8	7.07	53.6	Nil.....	Brown Stain.....	245.8	5
Run 19 2% in 10W Base Stock.....	1.8	6.27	10.1	Nil.....	Brassy.....	18.8	0
Run 19.5% in 10W Base Stock.....	15.0	10.08	77.1	Nil.....	do.....	199.1	4
PRODUCT FROM CONDENSATION OF DECENE-1 WITH BUTADIENE AND N-BUTYL MERCAPTAN							
Run 21.....	12.5	11.86	134	Nil.....	Light Brown.....	218.4	6

¹ Average values.

The results presented in Table II above, reveal that a solvent-refined Pennsylvania mineral oil, SAE 10W mineral oil base stock, which is considered in the art as a relatively stable mineral oil, has a stability number of 6-7 in the test described above. Similarly, the residual oil of run 20, obtained by condensation of decene-1 and styrene, without a thiol, has a stability number of 6; this is the residual oil having a cloud point of +60° F. In contrast, the residual oils of runs 6 and 10, obtained by condensation of decene-1 with styrene, and with n-butyl mercaptan and t-butyl mercaptan, respectively, are substantially more stable for they have stability ratings of zero. Residual oils of runs 12 and 13, obtained with thiophenol were less stable than those obtained with the butyl mercaptans, but were as stable as the mineral oil base stock. Stability numbers for runs 12 and 13 were 5 and 7 respectively. The oil obtained in run 14 with additional thiophenol, however, exhibits a substantially higher degree of stability than runs 12 and 13 inasmuch as its stability rating was 2. Oils obtained with thiophenethiol (runs 15 and 18) are somewhat superior in stability to those obtained with thiophenol. Here again, when a secondary reaction with more thiophenethiol was resorted to, an improvement in stability was realized (zero as compared with 3). This is shown by the oils of runs 15 and 16. In run 17 a larger amount of thiophenethiol was used in the initial reaction than was used in run 15, and a stability number of zero characterized the product. In run 19, still more thiophenethiol was used. The mineral oil base stock was effectively stabilized when 2% of the residual oil of run 19 was incorporated therein; however, 0.5 per cent of this residual oil was insufficient for this purpose. It will be recognized, therefore, that in all instances the new synthetic oils are equal to or better than an SAE 10W Pennsylvania motor oil in every respect.

As will be evident from the data presented above in Tables I and II, the condensation prod-

ucts of this invention are highly desirable lubricants per se. They are also of considerable value as blending agents for other lubricating oils. In view of the inherent stability of the synthetic oils, they impart stability to the oils with which they are blended. So also, they impart desirable viscosity index (V. I.) and pour point characteristics to the oils in combination therewith, for, as indicated above, they have advantageous viscosity index and pour point properties. In short, the synthetic oils find utility in "upgrading" other lubricants. Typical oils with which the synthetic oils may be blended are mineral oils such as are normally used in internal combustion and turbine engines. When so blended, the synthetic oils may comprise the major proportion of the final blended oil, or may even comprise a minor proportion thereof. For example, although used only in the amounts of the order of 1-10 per cent, the synthetic oils improve the stability of mineral oils, such as SAE 10 and 20 Pennsylvania type oils.

One or more of the individual properties of the synthetic lubricants of this invention may be further improved by incorporating therewith a small, but effective amount, of an addition agent such as an antioxidant, a detergent, an extreme pressure agent, a foam suppressor, a viscosity index (V. I.) improver, etc. Antioxidants are well-known in the art, and are generally characterized by phosphorus, sulfur, nitrogen, etc. content; representative of such materials is an oil-soluble, phosphorus- and sulfur-containing reaction product of pinene and phosphorus pentasulfide. Typical detergents which may be so used are metal salts of alkyl-substituted aromatic sulfonic or carboxylic acids, as illustrated by diwax benzene barium sulfonate and barium phenate, barium salt of a wax-substituted phenol carboxylic acid. Extreme pressure agents are well known; illustrating such materials are numerous chlorine and/or sulfur containing compositions, one such material being a chlornaphtha

xanthate. Silicones, such as dimethyl silicone, may be used to illustrate foam suppressing compositions. Viscosity index improving agents which may be used are typified by polypropylenes, polyisobutylenes, polyacrylate esters, and the like.

Contemplated also as within the scope of this invention is a method of lubricating relatively moving surfaces by maintaining therebetween a film consisting of any of the aforesaid oils.

It is to be understood that the foregoing description and representative examples are non-limiting and serve to illustrate the invention, which is to be broadly construed in the light of the language of the appended claims.

We claim:

1. The method of preparation of a viscous oil, which comprises: condensing, at a temperature between about 500° F. and about 800° F. for a period of time sufficient to effect condensation, one molar proportion of a normal, alpha mono-olefin having from five to eighteen carbon atoms per molecule, from about 0.01 to about one molar proportion of a conjugated olefinic hydrocarbon and from about 0.001 to about one molar proportion of a thiol.

2. The method of claim 1 wherein the temperature is between about 600° F. and about 750° F.

3. The method of claim 1 wherein the mono-olefin has from eight to twelve carbon atoms per molecule.

4. The method of claim 1 wherein the conjugated olefinic hydrocarbon is an alkenyl-substituted aromatic hydrocarbon.

5. The method of claim 1 wherein the conjugated olefinic hydrocarbon is a vinyl-substituted aromatic hydrocarbon.

6. The method of claim 1 wherein the thiol is an alkyl thiol.

7. The method of claim 1 wherein the thiol is an aryl thiol.

8. The method of claim 1 wherein the thiol is a heterocyclic thiol.

9. A new composition of matter comprising, a sulfur-containing condensation product obtained by: condensing, at a temperature between about 500° F. and about 800° F. for a period of time sufficient to effect condensation, one molar proportion of a normal, alpha mono-olefin having from five to eighteen carbon atoms per molecule, from about 0.01 to about one molar proportion of a conjugated olefinic hydrocarbon and from

about 0.001 to about one molar proportion of a thiol.

10. The composition of claim 9 wherein the temperature is between about 600° F. and about 750° F.

11. The composition of claim 9 wherein the mono-olefin has from eight to twelve carbon atoms per molecule.

12. The composition of claim 9 wherein the conjugated olefinic hydrocarbon is an alkenyl-substituted aromatic hydrocarbon.

13. The composition of claim 9 wherein the conjugated olefinic hydrocarbon is a vinyl-substituted aromatic hydrocarbon.

14. The composition of claim 9 wherein the thiol is an alkyl thiol.

15. The composition of claim 9 wherein the thiol is an aryl thiol.

16. The composition of claim 9 wherein the thiol is a heterocyclic thiol.

17. A sulfur-containing viscous oil of lubricating viscosity obtained by: condensing about 45 molar proportions of n-octene-1 with about 5.5 molar proportions of styrene and with one molar proportion of n-butyl thiol at about 600° F. for about ten hours.

18. A sulfur-containing viscous oil of lubricating viscosity obtained by: condensing about 45 molar proportions of n-decene-1 with about 5.5 molar proportions of styrene and with one molar proportion of t-butyl thiol at about 650° F. for about ten hours.

19. A sulfur-containing viscous oil of lubricating viscosity obtained by: condensing about 375 molar proportions of n-decene-1 with about 50 molar proportions of styrene and with one molar proportion of 3-thiophenethiol at about 600° F. for about ten hours.

WILLIAM E. GARWOOD.
JOHN W. BROOKS.
ALEXANDER N. SACHANEN.

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The following references are of record in the file of this patent:

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Certificate of Correction

March 14, 1950

Patent No. 2,500,672

WILLIAM E. GARWOOD ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 19, for "ankenyl" read *alkenyl*; columns 7 and 8, Table I, tenth column thereof, opposite "Run 17", for "0.936" read *0.9036*; columns 11 and 12, Table II, second column thereof, opposite "Run 12", for "12.3" read *13.3*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of December, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.