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METHOD OF PURIFYING A LUBRICATING OIL FEEDSTOCK WITH ZINC HALIDES

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THIS invention has to do with the preparation of synthetic lubricants from normal, alpha mono-olefins and, more particularly, has to do with the preparation of lubricants from certain complex mixtures containing such olefins.

As described in several related and co-pending applications, identified hereinafter, it has been found that normal, alpha mono-olefins of varied chain length can be converted to excellent synthetic lubricants. High viscosity indices, low pour points and/or superior stability characterize these lubricants. Not only have the individual normal, alpha mono-olefins proven of value in this regard, but mixtures of the same have been found to be satisfactory. In addition, complex mixtures containing substantial proportions of these olefins have been found to be suitable starting materials. A source for the complex mixtures containing these olefins is the Fischer-Tropsch process and related processes. As is well known in the art the Fischer-Tropsch process involves reaction of carbon monoxide and hydrogen in the presence of cobalt or chemically related catalysts, whereupon hydrocarbons, including olefins and paraffins, and oxygen-containing compounds are formed. When iron catalysts are used in place of cobalt, and/or when larger carbon monoxide to hydrogen ratios are used, larger quantities of oxygen-containing compounds are generally formed.

While the foregoing complex mixtures are converted to synthetic lubricants of low pour point, high viscosity index and good stability, as described in the applications referred to above, certain constituents therein are deleterious in reducing the yield and/or quality of the lubricants. Undesirable constituents include non-primary olefins, aromatics, naphthenes and paraffins; oxygen-containing compounds; suspended material, particularly metallic catalysts and their compounds. With regard to quality of the lubricants, it has been found that considerable color characterizes the lubricants. This is a serious shortcoming inasmuch as the highly colored lubricants generally do not respond to conventional procedures, namely, filtration, adsorption, etc., for removing color bodies. In addition, the carbon residue values of the lubricants are relatively high. A further shortcoming, traceable to constituents of the complex olefinic charge stocks, is that the viscosity indices of the lubricants generally fall below those of the lubricants formed from individual normal, alpha mono-olefins. Still another undesirable feature is in the relatively low response of the lubricants to inhibitors, particularly oxidation inhibitors. This is well illustrated with an outstanding oxidation inhibitor comprising an oil-soluble, phosphorus- and sul-

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fur-containing reaction product of pinene and phosphorus pentasulfide, which is described in detail in Patent No. 2,416,281 and in copending application Serial No. 482,482, filed April 9, 1943.

It has now been found that synthetic lubricants of good color and low carbon residues can be obtained by treating the foregoing complex olefin charge stocks with zinc chloride, distilling off the olefinic material from the resultant mixture and converting the olefinic material to synthetic lubricants by the procedures described in the following copending applications.

In copending application Serial No. 761,716, filed July 17, 1947, now abandoned in favor of application Serial No. 104,932, filed July 15, 1949, which matured into U. S. Letters Patent No. 2,500,166, issued March 14, 1950, it has been shown that normal, alpha mono-olefins having six to twelve carbon atoms per molecule form synthetic lubricants when heated at 500-750° F. in the absence of a catalyst (particularly of the Friedel-Crafts type). At temperatures of the order of 700-900° F., the use of a gas such as hydrogen, carbon monoxide and mixtures of such gases, with the aforesaid mono-olefins makes possible the formation of synthetic lubricants in substantial yield. This is described in copending application Serial Number 6,814, filed February 6, 1948, now Patent No. 2,500,159, issued March 14, 1950. The aforesaid mono-olefins are also converted to synthetic lubricants when contacted with lead tetra-acetate at elevated temperatures, particularly 400-700° F., as explained in copending application Serial Number 44,403, filed August 14, 1948, now Patent No. 2,500,161, issued March 14, 1950. Another related development involves condensation, at 500-750° F., of an olefin mixture comprising a short chain, mono-olefin of two to six carbon atoms and a long chain normal, alpha mono-olefin of ten to thirty carbon atoms; the mean carbon chain length is maintained within the range of six to twelve carbon atoms by proper proportioning of the olefins. This is described in copending application Serial Number 47,556 filed September 2, 1948, now Patent No. 2,500,162 issued March 14, 1950.

Polymerization of the aforesaid mono-olefins of six to fourteen carbon atoms per molecule, in the presence of a paraffin at temperatures in excess of 700° F., forms the subject matter of copending application Serial No. 86,384, filed April 8, 1949, now Patent No. 2,500,165 issued March 14, 1950. Monocyclic aromatics and/or naphthenes may be used in this polymerization, in place of the paraffin, as shown in copending application Serial No. 88,895, filed April 21, 1949, now Patent No. 2,500,244 issued March 14, 1950. Polymerization of said mono-olefins may also be

accomplished at temperatures within the range 550-750° F. by using small amounts of sulfur, selenium and/or tellurium; this is described in copending application Serial No. 63,204, filed December 2, 1948, now Patent No. 2,500,164 issued March 14, 1950. At temperatures of the order of 600-750° F., small amounts of phosphorus sulfides affect the polymerization of the aforesaid mono-olefins; this is described in copending application Serial No. 57,421, filed October 29, 1948, now Patent No. 2,500,163 issued March 14, 1950.

A catalytic conversion of normal, alpha mono-olefins having from five to eighteen carbon atoms to synthetic lubricants is described in copending application Serial No. 776,428, filed September 26, 1947, now abandoned; the catalysts used are silica-alumina composites.

Styrene also reacts with the aforesaid mono-olefins, at temperatures from about 500° F. to about 700° F. with the formation of synthetic lubricants, as shown in copending application Serial No. 6,993, filed February 7, 1948, now Patent No. 2,500,160 issued March 14, 1950. Conjugated hydrocarbons and sulfur react with normal, alpha mono-olefins having from about five to about eighteen carbon atoms to form lubricants; copending application Serial No. 33,438, filed June 16, 1948, now Patent No. 2,500,167 issued March 14, 1950. A related development involves reaction of conjugated hydrocarbons, phosphorus sulfides and the corresponding mono-olefins of six to fourteen carbon atoms, as shown in copending application Serial No. 64,904, filed December 11, 1948, now Patent No. 2,500,247 issued March 14, 1950. Still another related development is that wherein lubricants are formed by reaction of vinyl-substituted aromatic compounds, thiols and normal, alpha mono-olefins, described in copending application Serial No. 97,921, filed June 8, 1949, now Patent No. 2,500,672 issued March 14, 1950.

In copending application Serial No. 673,892, filed June 1, 1946, now Patent No. 2,551,638, issued May 8, 1951, it is shown that normal, alpha mono-olefins having from about seven to about twelve carbon atoms per molecule react with organic peroxides at 120-570° F. to form synthetic lubricants. With the corresponding mono-olefins of six to eighteen carbon chain length, organic peroxides and halogenated olefins are reacted at 120-570° F. with the formation of lubricants; Serial No. 776,427, filed September 26, 1947, now Patent No. 2,551,640, issued May 8, 1951. As a related development, organic peroxides, conjugated hydrocarbons and the aforesaid mono-olefins of from five to eighteen carbon atoms are reacted at 120-570° F. to form lubricants; Serial No. 53,372, filed October 7, 1948, now Patent No. 2,551,641, issued May 8, 1951. Organic peroxides, aromatic hydrocarbons and said mono-olefins of six to fourteen carbons also react to form lubricants, as described in copending application Serial No. 72,744 filed January 25, 1949, now Patent No. 2,551,642, issued May 8, 1951. Certain heterocyclic compounds may be used in place of the aromatic hydrocarbons in the last-mentioned development; this is explained in copending application Serial No. 83,772 filed March 26, 1949. Lubricants of high viscosity are formed by reacting the aforesaid mono-olefins of six to fourteen carbon atoms with certain unsaturated esters and organic peroxides; copending application Serial No. 72,745 filed September 23, 1949, now Patent No. 2,551,643 issued May 8, 1951.

Normal, alpha mono-olefins also react with olefinic mono-oxides and -sulfides at 500-700° F. to form lubricants, as explained in copending application Serial No. 750,170, filed May 23, 1947, now Patent No. 2,486,441 issued November 1, 1949.

It is to be understood, therefore, that the treated, complex olefinic charge may be converted to synthetic lubricants by any of the foregoing conversion procedures shown in the above-identified applications.

ZINC CHLORIDE TREAT

As indicated above, zinc chloride is used in treating the complex olefinic charge stock. Zinc fluoride, bromide and iodide are of the same chemical class as the chloride and may be used herein; however, in view of the much lower cost and greater availability of the chloride, the latter is most advantageous herein. The chloride is preferably used in anhydrous form, although satisfactory results are also obtained with a chloride containing some water. In fact, aqueous solutions of zinc chloride are suitable such as a saturated solution at 100° C. containing 615 grams ZnCl₂ per 100 parts of water; but, ordinarily, the water is removed by distillation in the treating procedure and is therefore not desired in the charge.

The amount of zinc chloride may be varied widely, depending upon the form of the chloride, the particular olefinic charge stock and the treating conditions. Quantities from about 0.5 per cent to 20 per cent or more of chloride, by weight, based upon the quantity of olefinic charge stock, are employed.

Treating temperatures may be varied considerably. Preferred, though, are temperatures of reflux of the olefinic charge, either at atmospheric, reduced or elevated pressure. Reflux temperatures make possible removal of any water of reaction, causing a more favorable equilibrium in various condensation and/or polymerization reactions catalyzed or induced by the solid acidic treating agent. Whatever the reaction mechanism, however, the olefinic content of the charge is not affected appreciably.

It will be clear that the zinc chloride treatment may be carried out in batch operation, as in a reaction vessel equipped with suitable distillation equipment. For example, the olefinic charge may be slowly distilled over the chloride, or may be heated with said compound for a longer period, e. g., several hours, and then flash distilled. It is also to be understood that the treat may be carried out in continuous operation, in which case the chloride and the olefinic charge stock may flow in concurrent or counter-current relationship to each other in a reaction vessel. It is preferred that the chloride be in finely-divided form in such operations. In all cases, agitation of the olefinic material and treating agent, or other means for providing intimate contact, is recommended.

Following treatment of the complex olefinic charge with zinc chloride, the treated charge is distilled. This distillation removes any reaction products which may dissolve in the excess hydrocarbon present. The distillate is a material containing purified and concentrated olefins, particularly normal, alpha mono-olefins. The distillate fraction boiling from about 100° F. to about 600° F., and boiling predominantly within the range 150-500° F., is taken overhead.

It will be apparent from the discussion of the

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zinc chloride treat and from the earlier discussion of the conversion processes contemplated herein that the treated olefinic charge stocks should contain normal, alpha mono-olefins having from about six to twelve, fourteen or eighteen carbon atoms depending upon the conversion procedure. Accordingly, the predominant portion of the treated olefinic mixture should boil above about 145° F., the boiling point of n-hexene-1, with the maximum boiling point of the treated mixture being not substantially greater than the boiling point of a normal, alpha mono-olefin of fourteen, sixteen or eighteen carbon atoms. It will also be apparent that the boiling range of the untreated olefinic mixture may be considerably wider than that of the treated mixture which is converted in the aforesaid procedures. The minimum boiling point may be well below that of the distillate fraction to be converted, and the maximum boiling point of the untreated mixture may be somewhat higher than said distillate fraction. With regard to the untreated mixture, it is generally advisable to subject the crude olefinic mixture from the Fischer-Tropsch process to a preliminary distillation, prior to the zinc chloride treat. In this distillation, gross contaminants such as iron particles and high boiling waxy materials are removed, and a distillate fraction of the selected boiling range is taken.

While filtration of the charge, prior to distillation, is not essential, it is a desirable procedure. With filtration, any occluded solid particles are removed.

In contrast to the zinc chloride treat and its influence upon the synthetic lubricants formed from the treated stocks are treatments with other metal halides. Calcium chloride, for example, has been found to be of little or no value in such a treat. While some improvement in viscosity index may be realized when calcium chloride is used, carbon residue and color values are gener-

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ally not improved. Aluminum chloride, which has been used considerably in hydrocarbon treatments, has proven to be undesirable in the procedure contemplated herein. As demonstrated hereinafter, AlCl₃ does not improve the color or carbon residue values, but actually has a deleterious effect. Ferric chloride, too, is of little value.

EXAMPLES

The following specific examples serve to illustrate, and not limit, the invention. In all examples, the olefin charge stocks used were obtained from Fischer-Tropsch reactions wherein iron catalysts were used. In Examples I-X, the charge stock had a boiling range of 200-300° F., a specific gravity of 0.7559, and contained a predominant quantity of normal, alpha mono-olefins of seven to nine carbon atoms; in Examples XI-XIV, the stock had a boiling range of 300-450° F., a specific gravity of 0.8003, and the mono-olefins were mainly of nine to twelve carbon atoms; and in Examples XV-XVI, the boiling range was 150-510° F., specific gravity, 0.7766, and the number of carbon atoms of said mono-olefins was from six to fourteen. The quantity of charge stock in each example was 500 parts by weight.

In the examples wherein a metal halide was used, the olefinic charge and the halide were mixed and the charge refluxed at atmospheric pressure for 1-4 hours, except as indicated otherwise. The mixture was vigorously stirred during refluxing and the refluxing was accompanied by water removal. The residual halide was removed by filtration and the filtrate was distilled. The distillate was then converted to a synthetic lubricant when heated in a bomb, at 625° or 650° F. as indicated, for ten hours in an atmosphere of nitrogen, as described in detail in said copending application Serial No. 761,716.

Pertinent data for the examples are set forth in Table I.

TABLE I
Pretreatment of olefinic charge stocks with metal halides

Run No.	I	II	III	IV	V	VI	VII	VIII
Boiling range of stock used, ° F.	200-300	200-300	200-300	200-300	200-300	200-300	200-300	200-300
Pretreatment	Filtered only.	Distilled only.	ZnCl ₂ (1%).	ZnCl ₂ (0.5%).	CaCl ₂ (17%).	CaCl ₂ +HCl (1%).	AlCl ₃ (1%).	AlCl ₃ (1%).
Temperature, ° C.			110	110	110	110	110	29 (liq.).
Time, hours			3	2	3	2½	1	2
Water removed, parts by weight.			3.0	2.2	1.8	1.8	4.0	None.
Redistillation, ° F.		200-294	200-290	200-294	200-300	200-280	200-300	200-302
Distillate color		Yellow	W. white	Yellow	Pale yellow	Pale yellow	Pale yellow	Yellow.
Material balance:								
Redistilled charge, percent.		91.5	76.0	89.0	80.0	79.0	89.0	62.0
Distillation residue, percent.		5.3	12.8	6.05	2.4	5.2	7.8	4.8
Total losses, percent.		3.2	11.2	4.95	17.6	15.8	3.2	33.2
Distillate inspections:								
Bromine number (Norwood).	98.9	101.8	99.9	97.7	104.8	100.7	99.5	102.4
Specific gravity	0.7559	0.7527	0.7491	0.7515	0.8348	0.7519	0.7519	0.7511
Conversion:								
Maximum pressure (PSI).	1,000	1,250	1,650	1,500	610	1,000	350	800
Oil yield, wt. percent of treated hydrocol charge.	20	18.5 ¹	17	11	22	15.4	11.5	18.9
Residual oil:								
Color, lovibond.	48	13	1.2	5.0	70	75	>750	590.
Carbon residue, Ramsbottom.	0.09	0.05	0.04	0.04	0.2	0.09	0.7	0.2.
Specific gravity	0.8591	0.8565	0.8408	0.8478	0.8448	0.8550	0.8681	0.8540.
Pour point, ° F.	<-30	<-30	<-35	<-30	<-35	<-30	<-30	<-35.
K. V. centistokes at—								
100° F.	21.23	21.50	12.25	17.96	10.09	20.84	20.53	19.69.
210° F.	4.04	4.08	2.96	3.69	2.62	4.06	3.82	3.92.
Viscosity index	92	96	104	99	102.3	105	73	103.

¹ Abnormal losses in bomb.

TABLE I—Continued
Pretreatment of olefinic charge stocks with metal halides

Run No.	IX	X	XI	XII	XIII	XIV	XV	XVI
Boiling range of stock used, ° F.	200-300	200-300	300-450	300-450	300-450	300-450	150-509	150-509
Pretreatment	FeCl ₃ (1%)	BF ₃ -ether (2.7%)	Refluxed and dist. 176.7 (liq.)	ZnCl ₂ (1%)	ZnCl ₂ (2%)	FeCl ₃ (1%)	None	ZnCl ₂ (1%)
Temperature, ° C	110	29 (liq.)	2	149	177 (liq.)	176.7 (liq.)		(2)
Time, hours	1	1	1.0	1	2	2		4
Water removed, parts by weight	2.9	None	2.0	2.0	2.0	2.0		
Redistillation, ° F	200-300	200-310	300-421	300-450	302-415	300-428		137-500
Distillate color	W. white	W. white	Yellow	Pale yellow	Pale yellow	V. P. yellow	None	V. P. yellow
Material balance:								
Redistilled charge, percent	89.0	86.0	87.4	91.3	86.0	78.3		89.7
Distillation residue, percent	5.0	5.4	9.65	5.75	7.35	6.0		8.3
Total losses, percent	6.0	8.6	2.95	2.95	6.65	15.7		2.0
Distillate inspections:								
Bromine number (Norwood)	101.9	101.0	73.4	72.6	71.1	71.4	91.7	93.9
Specific gravity	0.7519	0.7479	0.8003	0.7985	0.7985	0.8003	0.7766	0.7720
Conversion:								
Maximum pressure (PSI)	1,650	1,450	300	150	600	500	600	200
Oil yield, wt. percent of treated hydrocol charge	18.5	16	34.1	28.4	20.7	26	25.6	21
Residual oil:								
Color, lovibond	14	1.7	40	12	74	47	138	7
Carbon residue, Ramsbottom	0.09	0.07	0.1	0.07	0.1	0.1		0.04
Specific gravity	0.8453	0.8428	0.8692	0.8649	0.8649	0.8660	0.8783	0.8628
Pour point, ° F	<-35	-30	-30	<-30	<-30	<-30		<-30
K. V., centistokes at—								
100° F	14.49	17.24	19.86	18.85	20.72	17.95	33.89	28.09
210° F	3.23	3.65	3.96	3.90	4.11	3.76	5.33	4.87
Viscosity index	96	106	105.5	114	111.4	110	97.7	105.3

² Slow distillation over solid ZnCl₂, variable temperature.

Considering the foregoing data for Examples I-IV, it will be noted that the sequence of zinc chloride treat, distillation and conversion of distillate make possible the production of a superior lubricant. The example, the viscosity index values (V. I.) of the lubricants identified as Examples III and IV are 104 and 99, respectively; whereas, the V. I., of Examples I and II are only 92 and 96, respectively. In this connection, it should be noted that V. I. values are accurate to about ±2% (this includes normal variation in polymerization step, etc.). The data also reveal a substantial color improvement, 1.2 and 5.0 for the oils of Examples III and IV, respectively, compared with 48 and 13, respectively, for the oils of Examples I and II. Substantial reduction in carbon residue is also shown by Examples III and IV.

The effect of other metal halides is shown by Examples V-X. Calcium chloride is shown in Examples V and VI, demonstrating improvement in V. I. but less desirable color and carbon residue values. Examples VII and VIII reveal that aluminum chloride may have an adverse effect or an improving effect upon V. I., but greatly depreciates the color and carbon residue values. Ferric chloride is shown in Example IX; no improvement in carbon residue is realized and there is but slight improvement in V. I.

Examples XI-XIV involve a different fraction of olefinic stock, with the results similar in character to those of Examples I-X.

The value of slowly distilling an olefinic charge stock over zinc chloride is shown by Examples XV and XVI.

It is to be understood that the foregoing specific treating conditions and examples serve to illustrate the invention, for it will be apparent to those skilled in the art that modification and variations thereof may be used. It is to be understood, therefore, that such modifications and variations fall within the scope of the appended

claims, and that the invention is to be construed broadly in the light of the language of the claims.

We claim:

1. The process for preparing a synthetic lubricant having good color, low carbon residue and high viscosity index, which comprises: contacting with a zinc halide an olefinic charge stock obtained by a Fischer-Tropsch reaction, a substantial portion of said stock boiling within the range of about 150° F. to about 500° F.; distilling said treated stock and collecting an olefinic distillate boiling predominantly within the range of about 150° F. to about 500° F.; and converting said distillate into said synthetic lubricant.

2. The process of claim 1 wherein the halide is zinc chloride.

3. The process of claim 1 wherein the distillate is converted into said synthetic lubricant by heating the same at a temperature of about 625° F. for about ten hours.

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