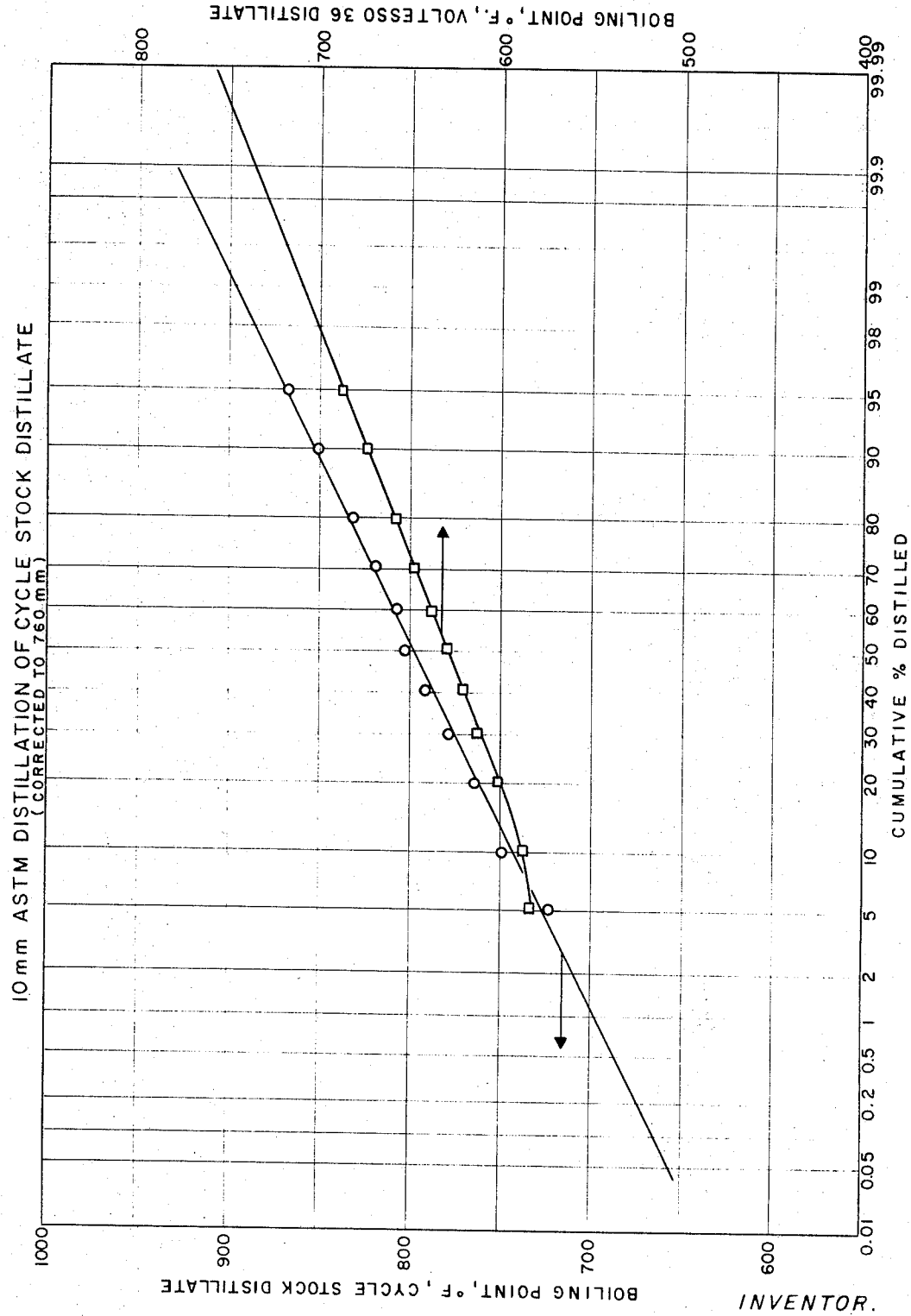
Dec. 29, 1970 J. G. LILLARD 3,551,324

TRANSFORMER OIL PRODUCTION BY ACETIC ACID EXTRACTION

Filed July 26, 1968



INVENTOR.
JAMES G. LILLARD,
BY Sylvester H. Brock, Jr.
ATTORNEY.

United States Patent Office 3,551,324
Patented Dec. 29, 1970

3,551,324

TRANSFORMER OIL PRODUCTION BY ACETIC ACID EXTRACTION

James G. Lillard, deceased, late of Baytown, Tex., by Thelma C. Lillard, executrix, 3200 Garth Road, Apt. 56, Baytown, Tex. 77520

Filed July 26, 1968, Ser. No. 749,912
Int. Cl. C10g 17/04, 21/16
U.S. Cl. 208—87 9 Claims

ABSTRACT OF THE DISCLOSURE

An improved transformer oil is obtained by subjecting a transformer oil base stock to extraction with concentrated acetic acid. Preferably, acetic acid containing no more than 5 weight percent of water will be employed at temperatures from 80 to 100° F. under conditions chosen to yield 90–95 volume percent raffinate. A solvent-to-oil ratio of 0.5 to 1.0 is preferred.

After-treatment may include hydrogenation and clay percolation.

The present invention relates to a novel method of producing oxidation-stable transformer oils. The present invention involves the use of an acetic acid extraction step in the sequence of treatment employed for producing transformer oils from base stocks known to be suitable for such use. As will be more fully hereinafter spelled out, the acetic acid treatment may be used at any one of several points in the treating sequence.

Transformer oils are commonly produced from highly naphthenic crude oil distillates, such as those which are obtained from Coastal crudes. One treating sequence may involve a distillation to obtain a stock of a suitable boiling range, hydrofining, SO_2 or phenol extraction, and percolation over Attapulgas clay. The process improvement of the present invention, acetic acid extraction, may be used anywhere in the treating sequence upstream of the clay percolation step, and the SO_2 extraction step may be omitted.

For example, the present invention may involve the acetic acid extraction of a Coastal distillate boiling within the range from 575° to 700° F. (corrected to 760 mm.) to obtain a raffinate portion amounting to from 85 to 97 weight percent of the feed to the extraction zone. The raffinate is then hydrofined at a temperature from 525° to 575° F. in contact with a cobalt molybdate catalyst and at a moderate hydrogen treat rate. The hydrofined product is then contacted with Attapulgas clay in order to provide a finished transformer oil product of acceptable oxidation stability.

The present invention can best be understood by advertence to the discussions below, wherein the various material variables are separately treated.

Feedstock: Any suitable transformer oil base stock can be used as a feedstock in the preesnt process. Exemplary of transformer oil feedstocks are the distillates which are obtained from Coastal crudes, such as a crude oil from the Webster Field in Harris County, Tex. The base transformer oil may comprise a single distillate, an admixture of distillates, or a distillate which has been modified by admixture with other oils such as catalytic cycle stock which has been dewaxed.

The crude distillate should boil within the range from about 550° F. to about 750° F., preferably within the range from about 575° to 700° F. Where a catalytic cycle stock is to be used (e.g., from 3 to 5 volume percent of mixture), the dewaxed catalytic cycle stock should boil within the range from 650° to 950° F., preferably from

700° to 910° F. The cycle stock is dewaxed by well-known procedures, such as MEK dewaxing.

The examples later given are based upon the use of a transformer oil base stock and a catalytic base stock distillate having the properties given below in Table I as exemplary of suitable feedstocks for use in the present invention.

TABLE I.—DISTILLATE INSPECTION DATA

	Base stock	Catalytic cycle oil
Gravity, ° API	28.1	18.7
Flash, COC, ° F	295	420
Viscosity at 100° F., S.S.U	58.8	193.5
Viscosity at 210° F., S.S.U		44.4
Color, Tag Robinson	6½	5½
Refractive index at 67° C	1.4701	1.5259
Refractive index at 20° C. N_D		1.55029
Silica gel aromatics		58.62
Saturates		40.38
Polar		1.00
Sulfur content, wt. percent	0.15	0.65
Neutralization No	1.16	0.06
Wax by SBA, wt. percent		14.0

Boiling curves (corrected to 760 mm.) for the base stock and catalytic cycle oil are shown in the drawing.

Solvent: The solvent of the present process is a glacial acetic acid, or concentrated acetic acid having no greater than 5 weight percent water. It has been found that concentrated acetic acid has a specificity for the removal of nitrogen compounds from transformer oils. Since hydrofining has also been shown to remove basic nitrogen compounds, it is seen that the use of the acetic acid extraction in combination with hydrofining allows the user to balance the extraction efficiency with the hydrogenation conditions so that for a light extraction (e.g., about 95% raffinate yield) more severe hydrogenating conditions will be employed (for example, 550–575° F.). Conversely, where a heavy extraction has taken place (about 85% raffinate yield), the lower temperatures (e.g., 525–540° F.) will be employed. Thus, it is seen that the particular feedstock can be tested and the optimum combination of extraction rigor and hydrogenation conditions can be easily determined.

Extraction: The extraction step is carried out as is well known in the art by one of many liquid contacting schemes; preferably a continuous, countercurrent, multiple-stage extraction will be carried out. Extraction conditions include: a temperature within the range from 75° to 250° F. (from 80–100° F. being preferred); atmospheric or superatmospheric pressures (not critical, atmospheric pressure being preferred); a solvent-to-oil volume ratio within the range from 0.5 to 1.0 (with a ratio of 1.0 being preferred); and extraction conditions being chosen to produce a raffinate product yield within the range from 85 volume percent to 97 volume percent of the original oil feed to the extraction zone, preferably a raffinate yield from 90 to 95 volume percent.

The process of the present invention has been compared to various other extraction processes for treating the transformer oil base stock, such as extraction with SO_2 and with sulfuric acid. Extraction with SO_2 and hydrogenation are each compared below with extraction with acetic acid.

TABLE II

	Percent of original (recovery)			
	Feed	Hydrogenation product	SO_2 raffinate	Acetic acid raffinate
Product yield	100	—(>95)	80	97
Sulfur	100	55	11	95+
Basic N_2	100	18	10	18

Note that all three processes reduce basic nitrogen, but acetic acid extraction does not remove sulfur-containing

compounds, many of which are natural oxidation inhibitors.

It has also been found that the conditions under which hydrogenation is carried out can be balanced against the extraction conditions to obtain a suitable product. In summary, the results of these experiments are given below.

TABLE III

Run Number	1	5	5a	5b
Solvent/oil ratio	½	1	1	1
Hydrofining temperature, ° F.[1]	540	525	550	575
Yield, vol. percent	99.0	83.1	83.1	83.1
Percent aromatics		21.7	20.8	20.0
Percent sulfur	0.06	0.02	0.02	0.02
Basic N_2, p.p.m.	2	5	1	1
Color/colorhold, Saybolt	+6/+5	+21/+21	+26/+25	+23/+21
Stability Tests:				
D-1904	(2)	(2)	(3)	(3)
D-1314	(2)	(2)	(3)	(3)
PFVO	(3)	(2)	(2)	(2)
Westinghouse (modified ASTM D-943)	(2)	(2)	(3)	(3)
Inhibitor response (ASTM D-1904, inhibited)		(2)	(2)	(2)

[1] Laboratory reactor—Nalcomo 471-1/16" extrudate; 1 v./v./hr.; 550 p.s.i.g.; 400 s.c.f. H_2/bbl. All products clay percolated at 2 gal./lb.
[2] Pass.
[3] Fail.

From the data given above, it is seen that the process of the present invention provides a novel way of obtaining a suitable transformer oil. The specificity for nitrogen compounds as opposed to sulfur compounds, exhibited by concentrated acetic acid, is nowhere duplicated in any of the other extraction agents. Thus, it is possible by using acetic acid as the extraction solvent to obtain from transformer oil base stocks a suitable and superior transformer oil product.

Finishing: The extracted base stock (raffinate) is finished hydrofining and clay treating. The hydrofining is preferably carried out in the presence of well-known hydrogenation catalysts such as nickel, platinum and cobalt molybdate. A preferred catalyst is cobalt molybdate supported on alumina and containing about 3.5 weight percent cobalt oxide and about 11.0 weight percent molybdenum oxide.

Hydrofining conditions will be correlated with the raffinate yield as aforesaid, and will generally fall within the following ranges:

Temperature: 525° to 625° F. (preferably 525° to 575° F.)
Pressure: 500 to 600 p.s.i.g. (preferably 550 p.s.i.g.)
Space velocity: 0.5 to 5 v./v./hr. (preferably 1.0 v./v./hr.)
Hydrogen rate: 200 to 500 s.c.f./bbl. (preferably 400 s.c.f./bbl.)

The hydrofined product is clay contacted (preferably by percolation), with adsorptive clays such as Attapulgas clay. A treat rate of about 2 gallons of oil per pound of clay has been found to be suitable, although from 1 to 5 gallons per pound should also be suitable.

In order to more fully disclose the basis of the present invention, the following examples are given.

EXAMPLES

Example 1

A transformer oil base stock as shown in Table I was extracted with glacial acetic acid. The extraction was 3-stage, countercurrent. Extraction conditions included a temperature of 75° F., atmospheric pressure and a solvent-to-oil ratio of 0.5 to obtain a raffinate yield of 97%. The raffinate was stripped under a nitrogen blanket and then hydrofined in contact with a Nalco 471 cobalt molybdate catalyst at a temperature of 540° F., a pressure of 560 p.s.i.g., a space velocity of 1.5 v./v./hr., and a hydrogen treat rate of 400 s.c.f. per barrel of oil charged. After the hydrogen treating, the oil was percolated over Attapulgas clay at a treat rate of 2 gallons of oil per pound of clay.

The finished oil (after clay treating) was subjected to a number of tests: ASTM D-1314 Sludge Test, ASTM D-1904, Power Factor Valued Oxidation (PFVO) and the Westinghouse modification of ASTM D-943. Data from these tests are shown below, with the target values for each test.

Stability test	Target	Test result	Evaluation
D-1904	72[2]		Pass.
D-1314[1]	0.075/0.15/0.30[3]	0.06/0.14/0.24	Pass.
PFVO	50[2]	50[4]	Marginal.
Westinghouse	100[2]	100+	Pass.

[1] Values for sludge at three days/seven days/fourteen days. Expressed as percent by weight based on the sample oil.
[2] Hours minimum.
[3] Maximum.
[4] Hours.

It is thought that raising the hydrofining temperature to 550° F. would have produced a suitable product.

Example 2

A transformer oil base stock as shown in Table I was admixed with a dewaxed catalytic cycle stock distillate as also shown in Table I. The catalytic cycle stock comprised 5 volume percent of the mixture. The mixture was extracted with glacial acetic acid as in Example 1, but through four stages; then the raffinate was stripped under a nitrogen blanket to a still temperature of 320° F. Raffinate yield was 95.8 volume percent.

The stripped raffinate was hydrofined in contact with cobalt molybdate catalyst at a temperature of 525° F., a pressure of 550 p.s.i.g., a space velocity of 1.0 v./v./hr., and a hydrogen treat rate of 400 s.c.f./bbl. The hydrofined oil was percolated over Attaplugas clay at the treat rate of 2 gallons per pound of clay.

The finished oil was subjected to a number of tests. Results are shown below.

Stability Test	Target	Test Result	Evaluation
D-1904, life hours	72[2]	<64[3]	Fail.
D-1314, sludge at 3 days/ 7 days/14 days	0.075/0.15/0.30	0.04/0.09/0.13	Pass.
PFVO	50[2]	>90[3]	Pass.
Westinghouse life	100[2]	>1,000[3]	Pass.
Inhibitor response[1]	600[2]	360+	Fail.

[1] D-1904, but oil is first inhibited with 0.15 weight percent of 1,3-di-tert butyl-2-hydroxy-5-methylbenzene, an oxidation inhibitor.
[2] Hours minimum.
[3] Hours.

The failure to meet the D-1904 and inhibitor response tests was thought to be attributable to the combination of low extraction (95.8 weight percent raffinate) and mild hydrofining (525° F.), and that a higher hydrofining temperature would have produced an acceptable product.

Example 3

A mixture of 97 volume percent transformer oil base with 3% cycle stock, each as shown in Table I. was sub-

jected to 6-stage extraction with glacial acetic acid at 75° F., atmospheric pressure, and a solvent-to-oil ratio of 1.0. A raffinate yield of 84.4 volume percent was obtained. The raffinate was hydrofined in contact with a cobalt molybdate catalyst at 525° F., 550 p.s.i.g., 1.0 v./v./hr., and 400 s.c.f./bbl. The hydrofined product was clay contacted to 2.0 gallon per pound. The finished oil passed all tests as is seen below:

Test	Target	Result, hours.	Evaluation.
D-1904 life	[1] 72	>72	Pass.
D-1314, sludge at 3 days/7 days/14 days	0.075/0.15/0.30	0.06/0.09/0.17	Do.
PFVO	[1] 50	>90	Do.
Westinghouse	[1] 100	>192	Do.
Inhibitor response	[1] 600	>672	Do.

[1] Hours minimum.

From Example 3 it is seen that an increase in the extraction severity (lowering raffinate yield from 95.8% to 84.4 volume percent) counteracted the low (525° F.) hydrofining temperature. The product passed all tests.

Example 4

A transformer oil base stock as shown in Table I was subjected to 6-stage countercurrent extraction with glacial acetic acid at 75° F., atmospheric pressure, and a solvent-to-oil ratio of 1.0, to a raffinate yield of 83.1%. The raffinate was split and hydrofined in contact with a cobalt molybdate catalyst at 525° F., 550° F., and 575° F., at a pressure of 550 p.s.i.g., a space velocity of 1.0 v./v./hr., and a hydrogen treat rate of 400 s.c.f./bbl. The catalyst in each case was Nalco 471. Hydrofined raffinate was clay treated to 2.0 gallons per pound. Results of testing are shown below.

Stability Test	Target	Result 525° F., hours	550° F., hours	575° F., hours
D-1904, life	[1] 72	>72	40	64
D-1314, sludge at 3 days/7 days/14 days	[2] 0.075/0.15/0.30	0.08/0.16/0.26	0.06/0.36/0.71	0.03/0.46/1.03
PFVO life	[1] 50	>90	>90	>90
Westinghouse	[1] 100	108	48	48
Inhibitor response	[1] 600	>672	[3] 504	720

[1] Hours, minimum.
[2] Maximum.
[3] Data questionable, may have passed.

From the data above, it is seen that the higher hydrofining temperature (550° F. and 575° F.) are unsuitable for heavily extracted oils (82.1% raffinate yield), but that the lower temperature (525° F.) in combination with heavy extraction produces a suitable product.

I claim:

1. In the production of a transformer oil from a transformer oil base stock boiling within the range from 550° F. to 750° F.,
the improvement of extracting said base stock with concentrated acetic acid containing not more than 5 weight percent of water
under conditions including:
a temperature from 75° F. to 250° F.,
a solvent/oil volume ratio from 0.5 to 1.0, and
a contact time chosen to produce a raffinate yield from 85 volume percent to 95 volume percent, based on oil feed,
and thereafter hydrogenating said raffinate in contact with a hydrogenation catalyst at
a temperature from 525° F. to 625° F.,
a pressure from 500 p.s.i.g. to 600 p.s.i.g.,
a space velocity from 0.5 to 5 v./v./hr., and
a hydrogen treat rate from 200 to 500 s.c.f./bbl.

2. A method in accordance with claim 1 wherein the acetic acid is glacial acetic acid, the temperature is from 80° F. to 100° F., the solvent/oil ratio is 1.0, and the raffinate yield is from 90 to 95 volume percent.

3. A method in accordance with claim 2 wherein the catalyst comprises 3.5 weight percent cobalt oxide and 11.0 weight percent molybdenum oxide on alumina.

4. In the production of a transformer oil from a transformer oil base stock boiling within the range from 550° F. to 750° F.,
the improvement of extracting said base stock with concentrated acetic acid containing not more than 5 weight percent of water
under conditions including:
a temperature from 75° F. to 250° F.,
a solvent/oil volume ratio from 0.5 to 1.0, and
a contact time chosen to produce a raffinate yield from 85 volume percent to 95 volume percent, base on oil feed,
thereafter hydrogenating said raffinate in contact with a hydrogenation catalyst at a temperature from 525° F. to 625° F., a pressure from 500 p.s.i.g. to 600 p.s.i.g., a space velocity from 0.5 to 5 v./v./hr., and a hydrogen rate from 200 to 500 s.c.f./bbl.,
wherein the catalyst comprises 3.5 weight percent cobalt oxide and 11.0 weight percent molybdenum oxide on alumina, and
wherein the feedstock to the extraction step contains from 0 to 5 volume percent of a catalytic cycle stock and from 97 to 95 volume percent Coastal distillate, said distillate and said catalytic cycle stock having the following characteristics:

	Distillate	Cycle stock
Boiling range, ° F	550-750	700-910
Gravity, ° API	28.1	18.7
Flash, COC, ° F	295	420
Viscosity 100° F., S.S.U	58.8	193.4
Viscosity 210° F., S.S.U		44.5
Color, Tag Robinson	6½	5/8
Silica gel aromatics		58.62
Saturates		40.38
Polar compounds		1.00

5. A method in accordance with claim 4 wherein the extraction solvent is glacial acetic acid and the extraction temperature is from 80° F. to 100° F., and the raffinate yield is from 90 volume percent to 95 volume percent.

6. A method in accordance with claim 5 wherein the hydrogenation temperature is from 525° F. to 550° F.

7. A method in accordance with claim 3 further comprising the step of percolating the hydrotreated oil over Attapulgas clay.

8. A method in accordance with claim 6 further comprising the step of percolating the hydrotreated oil over Attapulgas clay.

9. A method in accordance with claim 8 wherein the percolation treat rate is about 2 gallons of oil per pound of clay.

References Cited

UNITED STATES PATENTS

2,100,707	11/1937	Bhatnagar	208—328
2,288,373	6/1942	Smith et al.	208—14
2,984,617	5/1961	DeChellis et al.	208—90
3,252,887	5/1966	Rizzuti	208—14
3,406,111	10/1968	Wynkoop et al.	208—14

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—14, 90, 265, 328