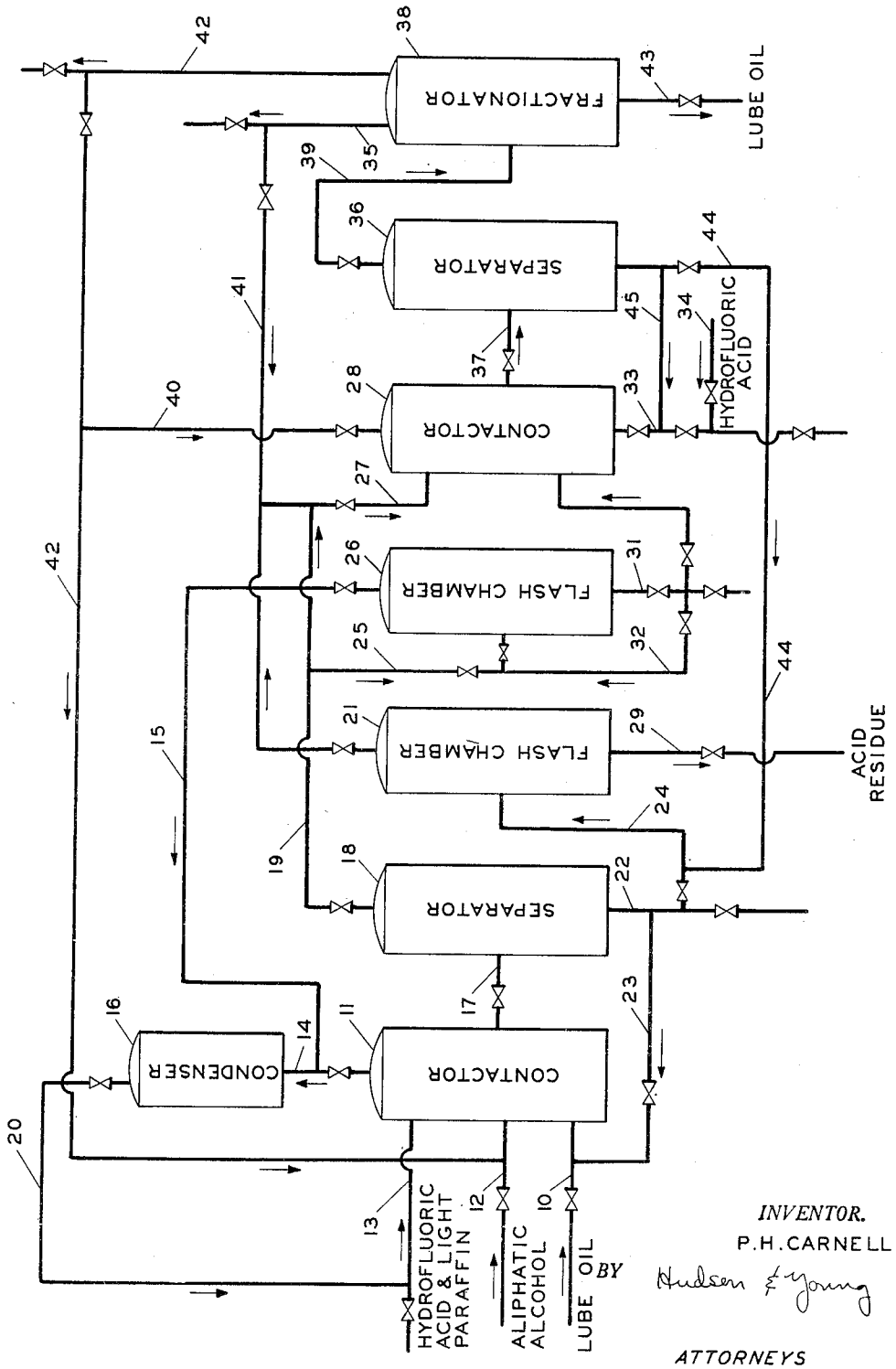
Nov. 14, 1950 P. H. CARNELL 2,529,484

TREATMENT FOR THE IMPROVEMENT OF LUBRICATING OILS

Filed Dec. 15, 1947



INVENTOR.
P. H. CARNELL
BY Hudson & Young
ATTORNEYS

Patented Nov. 14, 1950

2,529,484

UNITED STATES PATENT OFFICE

2,529,484

TREATMENT FOR THE IMPROVEMENT OF LUBRICATING OILS

Paul H. Carnell, Alma, Mich., assignor to Phillips Petroleum Company, a corporation of Delaware

Application December 15, 1947, Serial No. 791,801

7 Claims. (Cl. 196—13)

1

This invention relates to the treatment of lubricating oils to improve their properties. In one of its aspects it relates to the treatment of a natural or synthetic lubricating oil to effect an improvement in its properties. In another aspect it relates to the treatment of such an oil to increase its viscosity or viscosity index and/or to improve its color and stability.

I have discovered that treatment of lubricating oils with hydrofluoric acid and saturated aliphatic alcohols, at moderate temperatures, produces an improvement in the color, viscosity index, and stability of the oils. The improvement in color and viscosity index increases with the molecular weight of the alcohol used. In one embodiment of this invention the moderate temperature treatment, as stated above, may be followed by treatment with a similar mixture at elevated temperatures, improving still further the properties of the lubricating oil. In another embodiment of this invention, which still further improves the properties of the lubricating oil, the above procedure, as stated in the first embodiment, is followed by a third step, which comprises treating the lubricating oil at moderate temperatures with a mixture of hydrofluoric acid and aliphatic alcohols as was done in the first step.

In general this invention may be used to improve hydrocarbon materials within the range of lubricating oil constituents by contacting such hydrocarbon materials in the presence of hydrofluoric acid with at least one aliphatic alcohol having from 2 to 18, or more, carbon atoms per molecule. Especially beneficial effects are obtained with saturated aliphatic alcohols having 10 to 18 carbon atoms per molecule. Aliphatic alcohols are preferred to aromatic alcohols and phenols, because of the deasphaltizing properties of the former. In addition, treatment of hydrocarbon materials, and particularly of lubricating oils, with hydrofluoric acid-aliphatic alcohol mixtures produces greater improvement in the stability of the oils than is obtained when the oils are treated with mixtures of hydrofluoric acid and aromatic oxygen containing materials, such as, phenols and aromatic alcohols.

2

It is sometimes advantageous, when treating a lubricating oil with a mixture of hydrofluoric acid and a saturated aliphatic alcohol, to add a low-boiling paraffinic hydrocarbon material, such as propane, a butane, or a pentane, to the hydrofluoric acid-alcohol-oil mixture. Such a hydrocarbon material may act as a solvent to improve the separation of the oil and the hydrofluoric acid-alcohol layers, and may be used to control the temperature of the treating process by being allowed to evaporate during contacting.

In treating particular oils it is desirable to use hydrofluoric acid, a small amount of water, and a mixture of a major portion of a low molecular weight aliphatic alcohol, e.g., butanol, and a minor portion of the high molecular weight alcohol, e. g., octadecanol. Such treatment produces oils of improved color, stability, and viscosity-index. The solubility of the high molecular weight alcohol in the low molecular weight alcohol simplifies handling and recovery of the high molecular weight alcohol. High molecular weight alcohols as described herein are alcohols containing five or more carbon atoms.

The range of proportions of alcohol, oil, and hydrofluoric acid used when treating a mixed-base oil at relatively low temperatures is about 1:3:3 respectively, however, this may vary when treating other types of oil. The range of proportions of oil, alcohol, and hydrofluoric acid used when treating a mixed-base oil at elevated temperatures would be about 1:1:1 to about 1:1:3. Thus, the broad range of ratios is 1:1:1 to 1:3:3. When a mixture of a low molecular weight alcohol and a high molecular weight alcohol is used, the preferred proportion is from about 1:1 to 10:1, respectively. Usually the required volume of water is a product of dehydration of the alcohol with hydrofluoric acid, however, if this is not sufficient, additional water may be introduced with the alcohol. The proportion of water in the acid should not exceed about 10 weight per cent of the acid and, preferably, should not exceed about 5 weight per cent.

An object of this invention is to provide a new

process for improving the properties of lubricating oil.

Another object is to provide a method for improving natural lubricating oils.

A further object is to provide a method of improving mixed-base lubricating oils.

A further object is to provide a method of improving the viscosity index, color, and stability of natural or synthetic lubricating oils.

Other objects and advantages of my invention will be apparent from the accompanying disclosure and discussion.

Lubricating oil as referred to herein, includes all such products and their base stocks which have a viscosity of about 75 S. U. S. (Saybolt Universal Seconds) at 100° F., to about 150 S. U. S. at 210° F., and as are usually understood to be covered by this term by those skilled in the art. It includes particularly lubricating oil stocks such as a paraffin-base stock, a naphthene-base stock, a mixed-base stock, or a synthetic-base stock, which are refined for use as engine lubricants. By blending "neutrals" and "bright stocks," engine lubricating oils of varying viscosity and viscosity indices are produced.

An understanding of some of the many aspects of the invention may be aided by the attached drawing, which is a schematic flow diagram illustrating the invention in one of its embodiments.

Referring now to the drawing: In the initial step a lubricating oil is introduced through line **10** to contactor **11**; an aliphatic alcohol, preferably anhydrous, is introduced into the contactor through line **12**, and hydrofluoric acid and a low-boiling paraffinic material are introduced into the contactor through line **13**. A portion of the paraffinic material and hydrofluoric acid may be allowed to evaporate off through line **14** to condenser **16** as a means of temperature control. After a suitable contact time, of between about 5 and about 200 minutes, at a treating temperature, as high as 100° F. but preferably in the range of —20 to 40° F., in contactor **11**, the mixture is withdrawn through line **17** to separator **18**, in which the acid and hydrocarbon constituents separate into layers as by gravity.

From separator **18** the upper lubricating oil-paraffinic material layer is removed through lines **19** and **25** to flash chamber **26**. If desired, a portion of the lower acid layer may be recycled to contactor **11** through lines **22** and **23**, and the remaining portion removed through lines **22** and **24** to flash chamber **21**. Also the acid layer from separator **18** may be withdrawn through line **22**, to a purification system, not shown, if desired. From flash chamber **21**, an overhead product comprising hydrofluoric acid, water, and light hydrofluoric acid-soluble compounds is passed through lines **41** and **27** to contactor **28**. The acid-soluble residue from flash chamber **21** is withdrawn through line **29** as a kettle product. In flash chamber **26** the paraffinic solvent is flashed off the lubricating oil, which is passed through lines **31** and **32** to contactor **28** or recovered as a kettle product through line **31**. The solvent material from flash chamber **26** is recycled through line **15** to condenser **16** and through lines **20** and **13** to contactor **11**. If desired, the lubricating oil and solvent material may be passed directly from separator **18** to contactor **28** without first flashing off the solvent. The mixture in contactor **28**, containing hydrofluoric acid, water, lubricating oil, saturated aliphatic alcohols, and products of the process, is agitated at elevated temperatures between about 100 and about 500° F. and suitable pressures to keep the hydrofluoric acid substantially liquid, with possible polymerization, condensation, alkylation, and/or disproportionation taking place. The concentration of the hydrofluoric acid in contactor **28** must be at least 85 weight per cent. If the concentration of hydrofluoric acid gets below 85 weight per cent, the acid layer may be passed through line **33** to a separate fractionator not shown, the mixture distilled and the acid recovered; or anhydrous hydrofluoric acid may be added through line **34** as needed. From contactor **28**, lubricating oil, diluted hydrofluoric acid, saturated aliphatic alcohols, acid residue, and reaction products are passed to separator **36** through line **37**. The upper, lubricating oil, layer from separator **36** is passed to fractionator **38** through line **39** for distillation. Low molecular weight hydrocarbon compounds from fractionator **38** are recycled through lines **35**, **41**, and **27** to contactor **28**. A portion or all of these low molecular weight compounds may be removed through line **35**, when desired. Alcohols and other light reaction products from fractionator **38** may be recycled to contactor **11** through line **42**, or to contactor **28** through lines **42** and **40**. The lubricating oil is removed from fractionator **38** through line **43**. Said lubricating oil may be washed with caustic solution to remove small amounts of hydrofluoric acid if desired. The lower layer from separator **36**, containing hydrofluoric acid, water, acid residue, and products of the process, may be passed to flash chamber **21** through lines **44** and **24**, to contactor **28** through lines **44**, **45**, and **33**, or drawn off through line **44**. When a high molecular weight alcohol, e. g., octadecanol, is used, it is desirable to flash off the lower molecular weight alcohols and other light reaction products, leaving a mixture of high molecular weight alcohol and acid residue. The high molecular weight alcohol is then separated from the acid residue by extraction with a low molecular weight alcohol, which may be introduced in any one of several inlets.

Various valves, pumps, and other conventional equipment necessary for the successful practice of this invention will be familiar to one skilled in the art and have been omitted from the drawing for the sake of clarity.

As mentioned before, the process may be practiced by employing only the low-temperature treatment or by combination of the low-temperature and high-temperature steps, as described.

Following are specific examples of the treatment of lubricating oil with a mixture of hydrofluoric acid and o-cresol, and hydrofluoric acid and aliphatic alcohols. The procedure for runs 1 to 4 was as follows:

A steel bomb was charged with hydrofluoric acid, an alcohol, isopentane, and a mixed-base lubricating oil. The charged bomb was clamped to a platform rocker and agitated 120 minutes at room temperature. The bomb was removed from the rocker and placed in a vertical position, allowing the contents to settle. The acid and hydrocarbon layers were separated, and the hydrocarbon layer topped at reduced pressure to the initial boiling point of the untreated oil to remove the light ends. The physical data for the product oil were then determined.

The results of runs showing the benefits to be derived from the practice of this invention are shown in the following table, which lists the results of four combinations of treatment of mixed-base lubricating oils.

Run	Untreated Oil A	1	Untreated Oil B	2	3	4
HF, grams		613		922	962	949
Isopentane, grams		625		610	621	621
Alcohol		(1)		(2)	(3)	(4)
Alcohol, grams		314		245	249	247
Lube oil, grams		881		880	869	880
Test Data						
Viscosity, 100° F. SUS	287.3	282.5	343.9	352.0	344.4	334.4
Viscosity, 210° F. SUS	50.77	50.80	53.39	53.84	53.63	53.46
Viscosity Index (Dean & Davis)	89	92	86	86	88	
Pour Point, °F	+30	+20	+15	+15	+15	91
API Gravity	28.7	29.1	28.3	27.5	29.1	+10
ASTM Color	2½	1½	2½	3	2	29.0
						1½
Aluminum Block Stability Data						
Naphtha insolubles, wt. per cent: after heating	0.08	0.02	0.06	0.03	0.03	0.02
Neutralization number:						
before heating	0.00	0.01	0.04	0.02	0.00	0.00
after heating	0.33	0.54	0.17	0.10	0.07	0.06
Ramsbottom carbon residue, wt. per cent:						
before heating	0.02	0.06	0.01	-------	0.09	0.06
after heating	0.21	0.23	0.21	0.09	0.12	0.11
Evaporation loss, wt. per cent	4.3	3.7	2.0	1.2	1.3	1.7

[1] o-Cresol. [2] n-Butanol. [3] Decanol-1. [4] Octadecanol.

The data for the product oil of run 1 as compared to the data for untreated oil A show that hydrofluoric acid-cresol treatment of the oil produces an oil of improved viscosity index and color. However, the stability of the hydrofluoric acid-cresol treated oil is not as good as the untreated oil which is indicated by the higher neutralization number and carbon residue for the oil after heating in the aluminum block.

The data of run 2 when compared with the properties of an untreated lubricating oil B, in which the oil was treated with hydrofluoric acid and n-butanol, show improvement, primarily in stability.

Under the treating conditions of run 3 another sample of lubricating oil B, as compared with the untreated oil B, shows improvement in viscosity index, ASTM color, API gravity, and stability.

From comparison of data of run 4 with the untreated oil, it is seen that treating the lubricating oil with octadecanol and hydrofluoric acid improved viscosity index, pour point, API gravity, ASTM color, and stability.

It may be seen from the preceding examples that a lubricating oil is progressively improved in properties as the molecular weight of the aliphatic alcohol in the hydrofluoric acid-alcohol treating mixture is increased. A single treatment of a lubricating oil with hydrofluoric acid and one or more aliphatic alcohols at moderate temperatures improves the properties. Subsequent treating of a lubricating oil with a similar mixture of hydrofluoric acid and aliphatic alcohols at elevated temperatures followed by a third treating at moderate temperatures will increase still further the improvement of the properties of a lubricating oil.

Although the process has been described and exemplified in terms of its preferred modifications, it is understood that various changes may be made without departing from the spirit of the process as disclosed or from the scope of the claims.

I claim:

1. The process of manufacturing a lubricating oil of improved viscosity index, color, and stability which comprises contacting a lubricating oil by thorough mingling with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:3:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid and a temperature of about −20 to about 40° F., and further treating said lubricating oil with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:1:1 to about 1:1:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid and a temperature of about 100 to about 500° F., and recovering said improved lubricating oil.

2. The process of manufacturing a lubricating oil of improved viscosity index, color, and stability which comprises treating a lubricating oil by thorough mingling with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:1:1 to about 1:1:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid and a temperature of about 100 to about 500° F.; and further treating said lubricating oil with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:3:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid and a temperature of about −20 to about 40° F., recovering said improved lubricating oil.

3. A process of manufacturing a lubricating oil of improved viscosity index, color, and stability which comprises treating a lubricating oil by thorough mingling with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, a paraffinic material, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and

hydrofluoric acid of about 1:3:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid and a temperature of about −20 to about 40° F.; further treating said lubricating oil with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, a paraffinic material, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:1:1 to about 1:1:3 for about 5 to about 200 minutes at sufficient pressure to maintain the hydrofluoric acid substantially liquid and at a temperature of about 100 to about 500° F.; and further treating said lubricating oil with a mixture of at least one saturated aliphatic alcohol, hydrofluoric acid, a paraffinic material, and water not in excess of 5 to 10 weight per cent of the hydrofluoric acid present, in the proportion of alcohol, oil, and hydrofluoric acid of about 1:3:3 for about 5 to about 200 minutes at a sufficient pressure to maintain the hydrofluoric acid substantially liquid, and a temperature of about −20 to about 40° F., recovering said improved lubricating oil.

4. A process for the manufacture of improved lubricating oil which comprises contacting a lubricating oil with hydrofluoric acid and saturated aliphatic alcohol containing at least 10 carbon atoms per molecule at a temperature in the range of −20 to 100° F. and a contact time of 5 to 200 minutes, the ratio of alcohol to oil to hydrofluoric acid lying in the range of 1:1:1 to 1:3:3, and separating treating materials and acid soluble residue from the treated oil and recovering an improved lubricating oil as a product of the process.

5. A process for the manufacture of improved lubricating oil which comprises contacting a lubricating oil with hydrofluoric acid and saturated aliphatic alcohol containing 2 to 18 carbon atoms per molecule and comprising a major portion of C_2 to C_4 alcohol and a minor portion of C_5 to C_{18} alcohol in a ratio in the range of 1:1 to 10:1 respectively, treating said oil at a temperature in the range of −20 to 40° F. and a contact time of 5 to 200 minutes, the ratio of alcohol to oil to hydrofluoric acid lying in the range of 1:1:1 to 1:3:3, and separating treating materials and acid soluble residue from the treated oil and recovering an improved lubricating oil as a product of the process.

6. A process according to claim 5 wherein not more than 5 weight per cent of water based on hydrofluoric acid is present in the reaction mixture.

7. A process for the manufacture of lubricating oil of an improved viscosity index, color, and stability, which comprises contacting a lubricating oil with hydrofluoric acid and a saturated aliphatic alcohol containing 10 to 18 carbon atoms per molecule at a temperature in the range of −20 to 40° F. and a contact time of 5 to 200 minutes, the ratio of alcohol to oil to hydrofluoric acid lying in the range of 1:1:1 to 1:3:3, separating acid soluble residue from the mixture of treating and treated material and further treating said oil at a temperature in the range of 100 to 500° F., maintaining the concentration of hydrofluoric acid in the second treating step at not less than 85 weight per cent, separating treating materials from said oil and recovering an improved lubricating oil as a product of the process.

PAUL H. CARNELL.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,116,540	Roberts	May 10, 1938
2,288,853	Sowers	July 7, 1942
2,378,762	Frey	June 19, 1945
2,440,258	Elliott et al.	Apr. 27, 1948