June 27, 1944. E. LIEBER ET AL 2,352,213

LUBRICANT AND METHOD OF PREPARING SAME

Filed Oct. 1, 1940 3 Sheets-Sheet 1

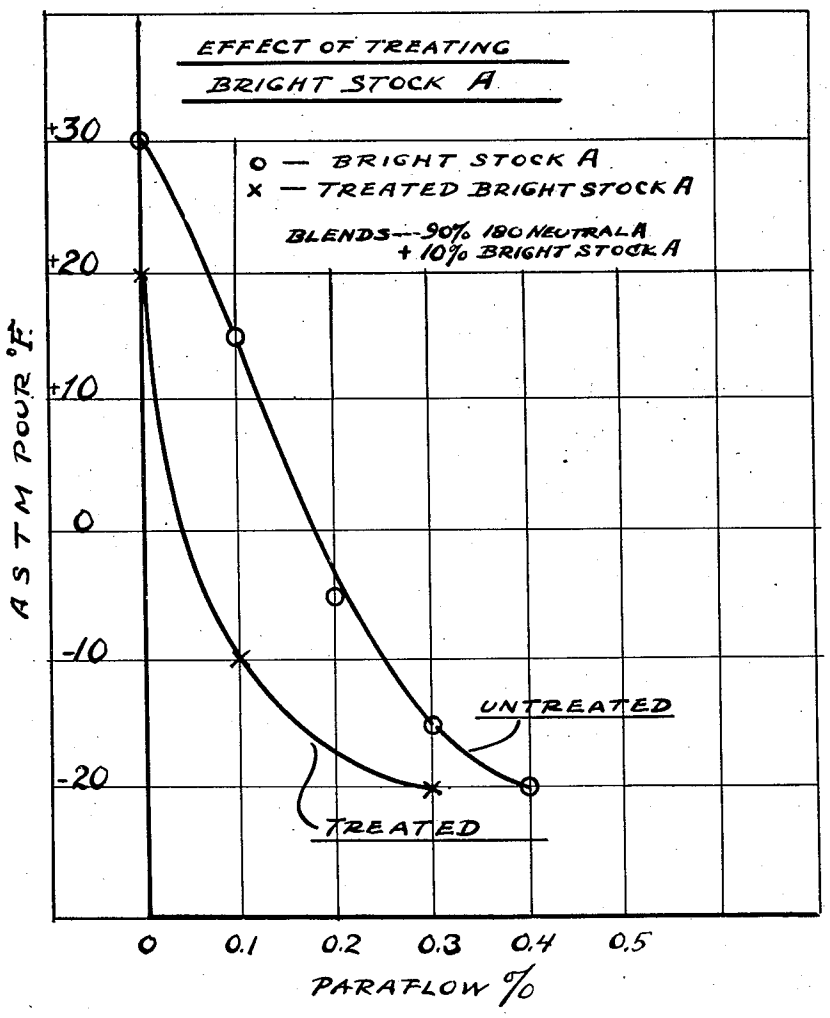


FIG.-1

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LUBRICANT AND METHOD OF PREPARING SAME

Filed Oct. 1, 1940 3 Sheets-Sheet 2

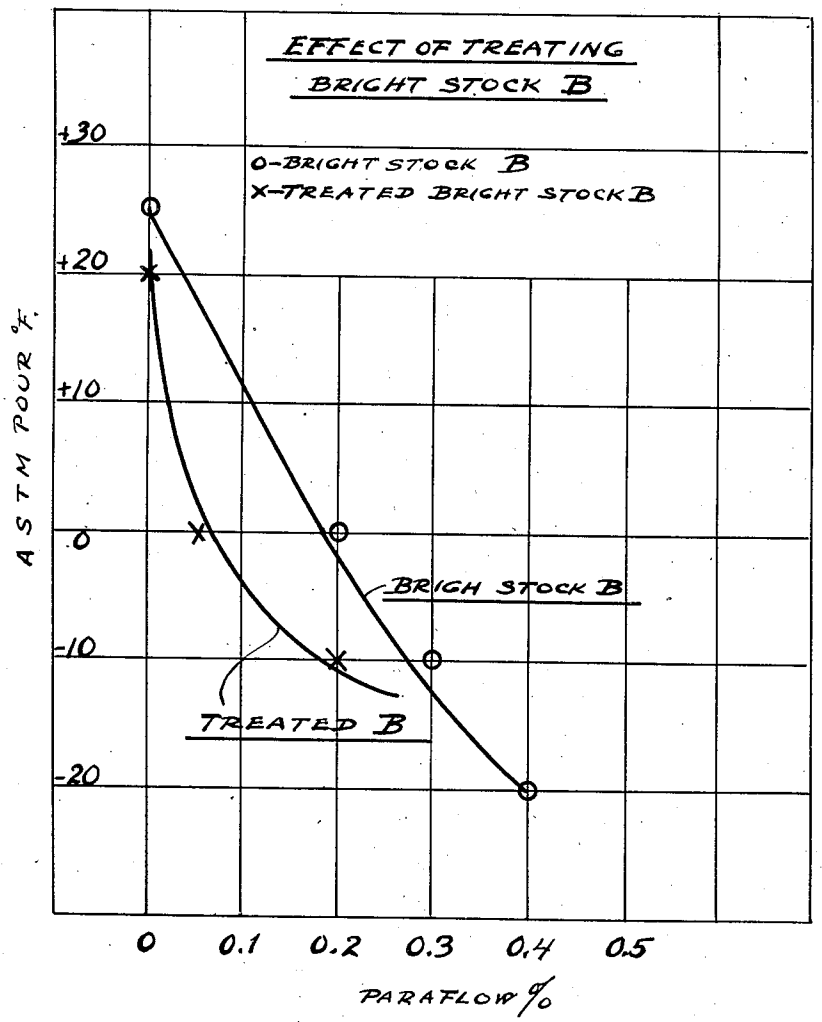


FIG.-2

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Filed Oct. 1, 1940 3 Sheets-Sheet 3

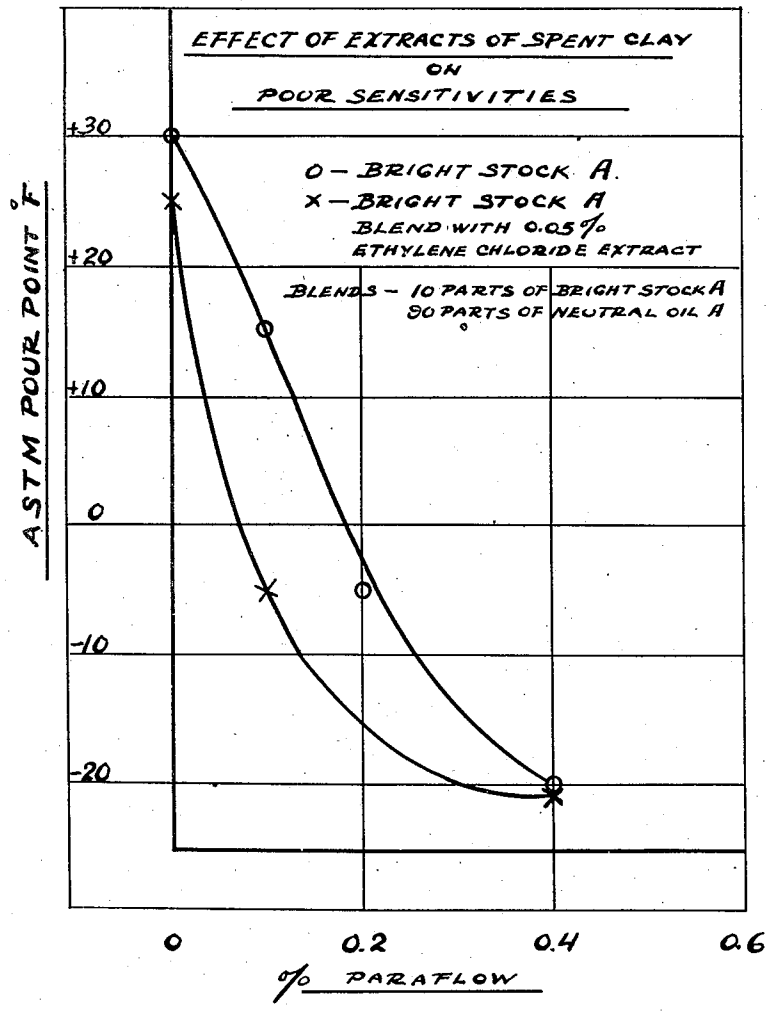


FIG.-3

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Patented June 27, 1944

UNITED STATES PATENT OFFICE

2,352,213

LUBRICANT AND METHOD OF PREPARING SAME

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Application October 1, 1940, Serial No. 359,190

8 Claims. (Cl. 196—151)

This invention relates to lubricants and to methods of reducing the pour point of waxy mineral lubricating oils.

It is already known that the pour point of a waxy mineral lubricating oil can be lowered or depressed by adding thereto a small amount of a synthetic hydrocarbon product formed by the condensation of a waxy hydrocarbon material with an aromatic hydrocarbon, as for instance, by condensing chlorinated paraffin wax with naphthalene in the presence of aluminum chloride as catalyst.

The present invention results from the discovery of the peculiar fact that spent or exhausted clays which have been used for clay treating lubricating oil stock, especially for percolation of crude cylinder stock, contain a substance which has the unexpected characteristics of increasing the sensitivity of a lubricant, especially a blend of a neutral oil and a Bright Stock, in which it is dissolved, to a reduction in pour point upon addition of a synthetic pour depressor such as the type mentioned above. This is a peculiar phenomenon because, in many instances, this substance, which for want of a better name will be referred to as a "pour susceptibility improver" or "pour sensitizer" does not actually reduce the pour point itself but merely increases the effectiveness of synthetic pour depressors which are added to blends containing this improver. This invention is, to some extent, contrary to various teachings of the prior art.

Broadly, therefore, the present invention comprises a lubricant comprising a waxy mineral lubricating oil, a small amount of a synthetic pour depressor, and a small amount of a natural pour sensitizer extracted from a petroleum hydrocarbon fraction, preferably a crude petroleum distillation bottoms, by suitable means such as by clay treating. The preferred method of incorporating this pour sensitizer into the lubricant is to prepare a naphtha solution of a portion of the lubricating oil to be used, preferably a Bright Stock, and then percolate this solution through the spent clay which has been used for clay treating a crude cylinder oil stock, and then evaporating off the volatile solvent from the treated solution and blending the resultant treated Bright Stock with any other lubricating oil stock to be used in the final blend. The pour depressor may either be added to the treated Bright Stock after removal of the solvent or may be added to any other oil such as a neutral oil, neutral distillate to be used in the final blend.

Although the above method of incorporating the pour sensitizer into the lubricant is preferred, because it produces a lubricant of better color and stability and substantially as good and even in some cases better quality as far as pour point reduction is concerned, however, other methods may be used, for instance, extracting the pour sensitizer from the spent clay by a volatile solvent such as benzene, removing the solvent and dissolving the resultant extract which is usually a black viscous oil containing our "pour sensitizer" as the experimental data will show below, to the Bright Stock or other mineral lubricating oil or blend to be used.

The spent clay to be used as the source of the pour sensitizer may be a clay which has been used for clay treating a crude cylinder oil stock preferably from a Pennsylvania type crude, although other crudes such as the Colombia crude of the naphthenic base type, or mixed base crudes may be used. The clay treating may be accomplished by any known method, such as percolation, or by clay contacting by which is meant dispersing the clay throughout the oil at the desired temperature and then separating the clay by suitable means such as by settling, filtering, centrifuging, etc. The temperature at which the clay treating should be carried out should be between the approximate limits of +50 and +250° F. Room temperature has been used with satisfactory results. The extent of the clay treating should be approximately that required to impart to the crude cylinder oil stock a color of at least 1 or 2 Robinson.

After the clay treating has been completed the spent clay may be either used as such or, and preferably, is washed substantially free of oil by rinsing with fresh naphtha, such as by percolating naphtha through the clay.

If the pour sensitizer in the spent clay is to be incorporated in the Bright Stock by direct contact as suggested above and which is our preferred method, the Bright Stock is preferably dissolved in 1 to 10 volumes, usually 2 to 5 volumes are sufficient, of a volatile solvent such as naphtha and then percolated, at room temperature through the spent clay which has been prepared as described above. The clay may be freed of adhering oil by rinsing with naphtha and the resultant washing may be combined with the main bulk of the naphtha solution. Then the combined naphtha percolate may be freed of solvent by distillation, e. g. on a water bath, preferably at reduced pressure, e. g. about 5 mm. absolute pressure. The temperature of this evaporation should preferably not exceed about 212° F. The treated Bright Stock thus obtained is ready for addition of the synthetic pour depressor to be used, together with any other oils to be blended therewith.

On the other hand, if it is not desired to contact the spent clay directly with the Bright Stock to be used in the finished lubricant, the spent clay, prepared as described above, may be

extracted by contacting therewith or percolating therethrough a suitable volatile solvent such as various hydrocarbon solvents, e. g. benzene, etc., or oxygen and chlorine derivatives of the hydrocarbons, e. g. acetone, ether, isopropyl alcohol, ethylene dichloride, and the like. In consideration of these solvents it should be noted that naphtha has been found valueless for extracting our "pour sensitizer" from the exhausted clay, and in fact is used for washing the treated clays in order to remove adhering oil before treatment for removal of "pour sensitizer." These solvents should be heated to a temperature not higher than about 150° F. to 200° F., although room temperature may be used, if desired. The extraction of the spent clay with the hot solvent is preferably continued until the drainings are substantially water white. The volatile solvent is then removed under vacuum, with some heating, if desired, although not at a temperature above about 212° F. The resulting extract is then dissolved in the Bright Stock to be used in the finished lubricant, the amount of this extract, which is the pour sensitizer, being about 0.1% to 10% by weight on the amount of Bright Stock, or about .01–1.0% on the finished lubricant.

The synthetic pour depressor to be used in the finished blend is preferably made by a Friedel-Crafts condensation of chlorinated paraffin wax, containing preferably about 10% to 15% of chlorine, with a suitable aromatic compound such as naphthalene, using about 13 to 15 parts by weight of naphthalene to 100 parts by weight of chlorinated paraffin wax, in the presence of about 0.5% to 10.0% of anhydrous aluminum chloride (based on the total weight of chlorinated wax), hydrolyzing the resulting product, removing the sludge and distilling off the low-boiling constituents from the condensation product, as by fire and steam up to a temperature of about 500° F. or 600° F. However, other synthetic pour depressors known to the art may be used if desired such as those described in the following patents; U. S. 2,018,758; 2,055,482; 2,087,682; 2,106,247; 2,115,823; 2,128,109; 2,161,987; 2,174,246; 2,201,767; 1,998,350; 2,033,546; 2,048,466; 2,053,853; 2,061,008; 2,077,068; 2,111,769; 2,114,812; 2,118,772; 2,130,024.

The amount of the synthetic pour depressor to be used will of course vary according to the nature of the lubricating oil stocks used, the amount of pour sensitizer used, the type and efficiency of the pour depressor, and the amount of pour reduction desired. Usually, however, it will range from about 0.01% to 10.0% and generally between the somewhat narrower limits of 0.05% and 2.0%. The invention appears to have its greatest effectiveness when the amount of synthetic pour depressor used is less than 0.5%, and the results are most astounding when the amount of pour depressor used is even less than 0.2% (by weight on the finished lubricant).

The accompanying drawings illustrate graphically the application of our invention.

The invention will be better understood from the following experimental data:

EXAMPLE 1

A series of tests was made in which the spent clay used was an Attapulgas #1 clay (30–60 mesh) which had been used for percolation of two different types of crude cylinder oil stock or distillation bottoms, one a Pennsylvania and the other a Colombian. The inspection and analytical data of the Pennsylvania crude bottoms were as follows:

TABLE 1

Analytical and inspection data on Pennsylvania Crude bottoms "A" cylinder stock

Gravity	°F.	25.6 at 60
Color		Black
Pour		+40 [1]
Vis./100	Saybolt seconds	2800
Vis./210	do	155
V. I.		89
Molecular weight		913
Per cent carbon		86.44
Per cent hydrogen		12.98
Acid number		0.08
Saponification number		1.89
24 hour sligh		19.6

[1] Average value.

250 grams of the Attapulgas clay were placed in a percolation tube and 200 cc. of the cylinder stock A (from the Pennsylvania crude) were dissolved in 800 cc. of naphtha and percolated through the clay until the color of the stock (after removal of the solvent) became a number 2 color on the Robinson scale. This required on the average 1 gram of fresh clay per gram of crude distillation bottoms. The spent clay was then washed free of oil by percolating 500 cc. of fresh naphtha through it. A similar procedure was used for clay percolation of the Colombian bottoms, although due to the asphaltic nature of the crude, about 2 grams of clay per gram of crude were required to bring about the same degree of decolorization. In each case, the spent clay was freed from oil by percolation with fresh naphtha.

In this series of tests, two different Bright Stocks were used, referred to herein as A and B. Bright Stock A had a pour point of +20° F. and B had a pour point of +15° F. although they were both obtained from Pennsylvania type crude oils, but prepared in different refineries. Also the lighter lubricating oils, with which the Bright Stocks were blended in making the finished lubricant, were two different neutral oils, also referred to herein as neutral oil A and neutral oil B, neutral A having a viscosity of 180 seconds Saybolt at 100° F., and a pour point of +30° F. and obtained from one refinery, and neutral B having a viscosity of 150 seconds Saybolt at 100° F. and a pour point of +25° F. and obtained from a different refinery.

In carrying out these tests the Bright Stock was taken up in 4 parts by volume of naphtha and percolated, at room temperature, through the spent clay, prepared as described above. After percolation, the clay was freed of adhering oil by rinsing with naphtha, and the combined naphtha percolates were freed of solvent by distillation on a water bath at 5 mm. mercury pressure. The treated Bright Stocks so recovered were blended in 10% concentration (by volume) in both the neutrals A and B and the pour points of the blend, both with and without pour depressor, were determined, the pour depressor used being made according to the general process mentioned above, but using specifically a chlorinated wax containing 10–12% chlorine, about 15 parts naphthalene, 1.5–3% of aluminum chloride, and a condensation temperature of at least 80–100° F. The experimental data obtained are summarized in Table 2.

TABLE 2

Treatment of Bright Stocks with spent clay

Test No.	Clay spent by crude	Bright Stock	Neutral	Pours on 10% treated B. S.+90% neutral, per cent pour depressor added					
				0.0	0.1	0.2	0.3	0.4	0.6
0	Blank	A	A	+30	+15	−5	−15	−20	−20
1a	Pennsylvania	A	A	+20	−10	−10	−20	−20	−25
1b [1]	do	A	A	+25	0	−10	−15	−20	−20
2	do	A	A	+25	−5	−10	−15	−20	−20
3	Blank	A	B	+25	+5	−5	−15	−20	−25
4	Pennsylvania	A	B	+5	−5	−10	−15	−20	−25
5	Colombian	A	A	+25	+5	−10	−15	------	------
6	Blank	B	A	+25	+10	0	−10	−20	−20
7	Pennsylvania	B	A	+25	−5	−10	−10	------	------
8	Blank	B	B	+25	+5	0	−10	−15	−20
9	Pennsylvania	B	B	+25	0	−10	−20	−20	−25
10	Blank on 150 neutral alone			+25	+10	0	−10	−15	−20

[1] Second pass through spent clay used in Test 1a.

From the data in the above Table 2 it is observed that the pour points of the neutral blends, without pour depressor, are practically the same as the original neutral oil. However, the neutral blend containing the treated Bright Stocks have become much more susceptible or sensitive to the pour depressor, especially in the lower concentration. It was also observed that inspection of the two Bright Stocks A and B, after treating in naphtha solutions, showed no change in the Robinson color thereof; however, the pour points of the original Bright Stocks tended to increase as shown by the following data:

	Pour point °F. of Bright Stock	
	A	B
Original	+20	+15
Treated	+40	+20

As already indicated from the data in Table 2 that, with one exception, the treated Bright Stocks—neutral blend, without pour depressor, have substantially the same pour point as the neutral oil alone. One exception, however, was noted in Test 4 where the pour point of the neutral oil was +25° F. and the pour point of the Bright Stock was +40° F. but the blend of 90% neutral and 10% Bright Stock was +5° F. This is quite unexpected, especially since the untreated Bright Stock alone had a pour point of +20° F. so that even though the treatment of the Bright Stock raised the pour point from +20° F. to +40° F., the blending with the neutral gave a substantial reduction in pour point, down to +5° F. instead of +25° F.

It is also noted from Table 2 that the spent clay used for treating the Colombian crude bottoms yielded a somewhat less potent Bright Stock A than that obtained by percolating the same Bright Stock through clay that had been used for treating a Pennsylvania crude.

It will also be noted by comparing Tests 0 and 1 in Table 2 that the treated Bright Stock (in Test 1—A effected the greatest decrease in pour point when 0.1% of pour depressor was used), namely, from +15 to −10° F., a lowering of the pour point by 25 degrees whereas with larger additions of pour depressor, e. g. 0.2% to 0.6%, although the actual pour point was lower, the difference in pour point between that with the untreated Bright Stock and with the treated Bright Stock (comparing Tests 0 and 1—A) was only about 5 degrees. These results are set forth graphically in Fig. 1 which emphasizes clearly the advantages of this invention.

Similarly, with Bright Stock B in Tests 6 and 7 the greatest difference in pour point occurred with the use of 0.1% of pour depressor, thus indicating that the invention is especially useful for amounts of pour depressor less than 0.2%. The results of these Tests 6 and 7 are set forth graphically in Fig. 2.

EXAMPLE 2

For another test, 500 cc. of Pennsylvania crude bottoms, dissolved in 1500 cc. of a refined naphtha marketed under trade name "Varsol," which was clay percolated before use, were percolated through three successive 200 gram portions of Number 1 freshly activated Attapulgas clay. The filtrate, after removal of the solvent, yielded 420 cc. of stock having a No. 1 Robinson color and having a pour point of +90° F. (This is an increase of +50° F. over the original stock.) This yield of clay-percolated oil amounted to 84% of the original. The spent clay, after washing with light naphtha, was placed in a Soxhlet apparatus and extracted with hot benzol until the draining ran water white. The benzol was then removed under high vacuum on a water bath at a temperature not exceeding 212° F. 65 cc. (13% by volume) of a very viscous black oil was obtained as distillation residue, thus indicating that whereas the spent clay had at first contained about 16% of the original Pennsylvania crude bottoms, after the extraction with hot benzol, the spent clay only retains about 3% of the original Pennsylvania crude bottoms. This viscous black oil extract, containing the "pour sensitizer" of this invention, was blended with the same Bright Stock A used in the previous test, and the pour points of the resulting blends were determined as follows:

TABLE 3

	Pour point, °F.
Bright Stock A	+20
Bright Stock A+0.5% extract (pour sensitizer)	+20
Bright Stock A+1.0% extract (pour sensitizer)	+20
Bright Stock A+2.0% extract (pour sensitizer)	+20
Bright Stock A+0.5% pour depressor [1]	0

[1] The same pour depressor as used in Example 1.

It is noted that the extract, which contains the pour sensitizer has no effect at all on the pour point of the Bright Stock, when added thereto in concentrations of from 0.5% to 2%. The last test in Table 3 was added merely to show that the addition of a true pour depressor does reduce the pour points of this same Bright Stock, 0.5% of the pour depressor reducing it from 20° F. to 0° F. It should be noted that the extract caused a considerable darkening of the Bright Stock A into which it was blended; and since in the previous procedure (Example 1) no change in color of the Bright Stock was effected, this leads to the conclusion that the extract contains the novel "pour sensitizer" and that the dark coloring matter of the extracts has no effect.

Now to determine the pour sensitizing effects of this extract, 10 parts by volume of Bright Stock A containing 0.5% (by weight) of the benzol extract of the spent clay, were blended in 90 parts by volume of neutral A. This corresponds to 0.05% of the benzol extract in the finished blend. Pour points, with and without pour depressor (the same one as used in Example 1), were then determined, the data obtained being shown in Table 4.

TABLE 4

Per cent pour depressor added to	Pour points, °F.	
	10% B. S. A., 90% 180 neut. A	10% treated B. S. A., 90% 180 neut. A
0.0	+30	+30
0.1	+15	0
0.2	−10	−10
0.3	−15	−20

It is noted from these results in Table 4 that the treated Bright Stock A (containing the pour sensitizer) did not reduce the 30° F. pour point of the bright stock neutral blend when no pour depressor was used; on the other hand, the addition of 0.1% of pour depressor caused a remarkable change in the results, effecting a 30° reduction in pour point in the blend containing the treated Bright Stock but only a 15° reduction in pour point in the blend not containing any of the pour sensitizer. With larger additions of pour depressor, this pour sensitizing effect continues, although to a less noticeable extent.

EXAMPLE 3

The procedure used in Example 2 was repeated except for the substitution of a number of other solvents, instead of the benzene, in order to compare the relative pour sensitizing potency of the extract obtained with different types of solvents. A large quantity of No. 1 fresh Attapulgas clay was spent by percolating Pennsylvania crude bottoms through it in the same manner as described above. This spent clay was then divided into aliquot portions and extracted in a Soxhlet extraction apparatus with hot solvent until the drainings ran clear, using ethylene dichloride, acetone, ethyl ether and isopropyl alcohol respectively as the solvents. The yields of extracts from 300 grams of spent clay (using approximately the same ratio of crude bottoms to clay as in Example 2) for each solvent were approximately the same, namely, about 12 grams.

Each extract was tested for true pour depressing properties, as was done in Example 2, namely, by adding 0.5%, 1.0%, and 2.0%, respectively, of each different extract to the Bright Stock A, having an original pour point of +20° F., but in every single case the pour point of the Bright Stock containing the small addition of extract was identically the same, namely, +20° F. This shows that none of the extracts had any pour-reducing effect on this Bright Stock.

These same extracts were then made up in blends with 10 volumes of Bright Stock and 90 volumes of neutral A, using three different amounts, namely, 0.05%, 0.10%, and 0.20% of each extract in the final blend, and then the pour points of these blends were determined with and without addition of pour depressor (the one used in Example 1). The results are shown in the following Table 5.

TABLE 5

Test No.	Solvent used for extraction	Pour sensitizer	Pour points, °F., per cent pour depressor				
			0.0	0.1	0.2	0.3	0.4
1	None	None	+30	+15	−5	−15	−20
2	Ethylene dichloride	0.05	+25	−5	−10	−15	−20
3	do	0.10	+25	−5	−10	−15	−20
4	do	0.20	+25	−5	−15	−20	−25
5	Acetone	0.05	+25	0	−10	−15	−20
6	do	0.10	+25	−5	−10	−15	−20
7	do	0.20	+25	−5	−10	−15	−20
8	Ethyl ether	0.05	+25	+10	−10	−15	−20
9	do	0.10	+25	−5	−10	−15	−20
10	do	0.20	+25	−5	−10	−15	−20
11	Isopropyl alcohol	0.05	+25	+10	−10	−15	−20
12	do	0.10	+25	+10	−10	−15	−20
13	do	0.20	+25	0	−10	−20	−20

It is remarkable to observe the results in Table 5 that the pour points of all of the blends, Tests 1–13, were substantially identical in the columns representing an addition of 0 pour depressor or 0.4% and 0.3% pour depressor, and that even with 0.2% of pour depressor only slight changes were noticeable, but that in the column representing an addition of 0.1% of pour depressor quite remarkable reductions in pour point were effected, due to the "pour sensitizing" effect of the extracts obtained by the various solvents, especially with the ethylene dichloride and acetone. The extracts obtained by the ethyl ether

and isopropyl alcohol were quite effective when used in the larger amounts, e. g. 0.2%, but not so effective in the small amounts, such as 0.05%. The most surprising result of all was in Test 2 where 0.05% of pour sensitizer obtained by extracting the spent clay with ethylene dichloride was used, thus enabling an addition of 0.1% of pour depressor to obtain a pour point of —5° F., whereas the same amount of pour depressor only obtained a pour point of +15° F. in the absence of the pour sensitizer (in Test 1). The results of Tests 1 and 2 are compared graphically in Fig. 3.

In comparing the two methods of sensitizing oils to pour depressors discussed above, it should be kept in mind that they differ in several respects. Thus, the more direct method of percolating the Bright Stock itself (in naphtha solution) through the spent clay yields a product which, while it sometimes increases in pour point, has suffered no change in color. The clay extracts, on the other hand, markedly darken the oils into which they are blended.

Although the theory of the mechanism of the operation of the present invention is not at all understood, the results are clear and certain, and are highly unexpected, especially in the range of low concentrations of pour depressor.

It is not intended that this invention be limited by the specific examples which have been given here merely for the sake of illustration nor by any theory as to the mechanism of the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. A lubricant comprising a waxy mineral lubricating oil, a small amount of synthetic pour depressor, and a small amount of natural pour sensitizer extracted from a crude petroleum distillation bottoms by clay treating.

2. Composition according to claim 1 in which the mineral lubricating oil is a blend of a lubricating oil distillate and a refined residual.

3. Composition according to claim 1 in which the pour depressor is made by condensing long aliphatic hydrocarbon chains onto an aromatic nucleus.

4. A lubricating oil composition comprising a major proportion of waxy mineral lubricating oil containing about 50% to 95% by volume of refined lubricating oil distillate having a viscosity of about 100–1000 seconds Saybolt at 100° F., and about 50 to 5% by volume of Bright Stock, said composition also containing about 0.01%–5.0% by weight of the total blend of a pour depressor made by condensing chlorinated paraffin wax with naphthalene in the presence of aluminum chloride, and also containing a small amount of a pour sensitizer extracted from a crude cylinder stock by clay treating.

5. Composition according to claim 4, in which the pour sensitizer has been removed from the clay used for said clay treating by contacting said clay with a naphtha solution of at least a portion of the Bright Stock to be used in the finished lubricating oil composition.

6. Composition according to claim 4, in which the pour sensitizer has been removed from the clay used for the clay treating, by extraction of said spent clay by a volatile solvent, separated from said solvent by distillation at a temperature not substantially above 212° F., and then dissolved in the lubricant to the extent of about 0.01%–1.0% by weight on the finished blend.

7. Composition according to claim 4, in which the pour sensitizer was obtained from a Pennsylvania type crude oil stock.

8. The process of preparing lubricating oil compositions which comprises percolating Pennsylvania crude petroleum distillation bottoms through freshly activated Attapulgas clay, washing the resultant spent clay with a small amount of naphtha, then contacting the residual washed spent clay with a naphtha solution of Bright Stock to permit said Bright Stock solution to dissolve some of the constituents present in the spent clay having pour sensitizing properties, removing the naphtha from said Bright Stock solution and blending said treated Bright Stock with a lower viscosity refined lubricating oil distillate, and also incorporating in the finished blend a small amount of synthetic pour depressor.

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