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POUR POINT DEPRESSANT FOR
LUBRICATING OILSIsador Silverman, Newark, N. J., assignor to L.
Sonneborn Sons, Inc., a corporation of Dela-
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8 Claims. (Cl. 252-36)

This invention relates to new and useful improvements in pour point depressants for lubricating oils.

Metal soaps, such as palmitates, oleates and stearates, and particularly the aluminum soaps, such as the aluminum stearates, have in the past been used as pour point depressants for waxy petroleum hydrocarbon oils having a relatively high pour point due to the wax contained therein. The use of these depressants, however, is attended by the disadvantage that the pour point obtained is substantially fugitive and reverts upon storage or in service progressively towards the pour point of the original undepressed oil.

I have discovered that this disadvantage may be overcome and that a substantially permanent lowering of the pour point and a substantially non-fugitive, non-reverting pour point may be obtained by admixing with the oil a metallic soap depressant in the presence of an oil soluble petroleum sulphonate.

The metal stearates conventionally used as pour point depressants, and particularly the tin, titanium, calcium, magnesium and aluminum stearates, constitute satisfactory depressants in accordance with the invention. They may be used either singly or in mixture with one another. Though the use of one or the other particular stearate may be recommended by special circumstances or considerations, as for instance, the use of tin stearate in cases where anti-corrosive properties are desired, the use of aluminum stearate in most instances is the preferred practice. The metal stearate should be soluble in hydrocarbon oil and the valence of its metal radical should be at least two and preferably three.

Where in the specification and claims reference is made to the term "metallic soap pour point depressant of the stearate type" or where an expression of similar import is used, it is intended to designate thereby any oil soluble metallic soap, such as a palmitate, stearate, oleate or the like, capable of depressing the pour point of a waxy lubricating oil, the normal relatively high pour point of which is due to the wax contained therein, and typified by the conventionally used oil soluble metal stearates and particularly aluminum stearate.

The oil soluble petroleum sulphonate that may be used within the purview of my invention may be any one or more of the oil soluble metal sulphonates derived from the sulphonation of petroleum hydrocarbons. The oil soluble sulphonate may constitute either an individual sulphonated petroleum hydrocarbon or a mixture or combination of said sulphonated petroleum hydrocarbons. I prefer, however, to use as the oil soluble sulphonate in accordance with my invention, a combination or mixture of such sulphonated petroleum hydrocarbons. The most

convenient source for such a combination or mixture of sulphonated petroleum hydrocarbons is furnished by the so-termed "mahogany petroleum sulphonic acids" obtained in the acid refining of petroleum oil distillates with concentrated and preferably fuming sulphuric acid under sulphonating conditions of acid concentration and temperature, and isolated from the petroleum oil layer, after the separation of the acid sludge, in the form of their salts, i. e., mahogany petroleum sulphonates or oil soluble petroleum sulphonates in accordance with well-known practices. Suitable oil soluble metal petroleum sulphonates are, for instance, the sodium, potassium, magnesium, zinc, nickel, cobalt, cadmium, tin, chromium, and aluminum sulphonates. Ammonium sulphonates may also be used though their addition is not recommended in many cases on account of their heat instability which may entail the formation of deleterious free acidity. In the majority of cases, however, the tin and aluminum sulphonates are preferred. The tin, cobalt and cadmium petroleum sulphonates have the added advantage that they will impart, to an appreciable degree, anti-corrosive properties to any hydrocarbon oil product containing the same.

For best results I have found it of advantage and prefer to use an oil soluble petroleum sulphonate that has been substantially freed from inorganic impurities and free organic acidity. Though I preferably use in accordance with my invention a combination or mixture of sulphonated compounds obtained from mahogany petroleum sulphonic acid or their salts, it is possible and sometimes of advantage to use as the oil soluble petroleum sulphonate in accordance with the invention, one or more fractions or component ingredients of the mahogany petroleum sulphonates.

The depressant in accordance with the invention may be conveniently prepared by intimately mixing a conventional metallic soap depressant with the required amount of oil soluble petroleum sulphonate. In most cases I prefer a ratio of metallic soap such as stearate to sulphonate from 10:1 to 2:1, the latter being the most efficient proportion; although the amount of sulphonate present in the lowest effective ratio of metallic soap to sulphonate of 10:1 is relatively small it nevertheless suffices to substantially eliminate any reversion of the pour point of the waxy hydrocarbon oil.

The oil soluble petroleum sulphonate may be used either as such, that is, in substantially dry condition, or in the form of a solution in a suitable solvent such as a petroleum hydrocarbon oil. When using mahogany petroleum sulphonate in accordance with the invention, I prefer a solution in a suitable oil and preferably in what is termed "retained oil" as such solution is the

conventional product ordinarily and conveniently obtained in the manufacture of these substances.

The expression "oil soluble petroleum sulphonate" or any term of similar import, as employed in the specification and claims, connotes generically any one or more oil soluble metal salts of a sulphonated hydrocarbon or mixture of hydrocarbons within the petroleum hydrocarbon range and irrespective of whether the same is a mahogany petroleum sulphonate compound or fraction thereof, or not.

For the purpose of depressing the pour point of a paraffin base oil such as a Pennsylvania grade oil, so much of the depressant prepared in accordance with the invention is added thereto as is equivalent to an amount of oil soluble metallic soap sufficient to appreciably reduce the pour point of the oil and preferably reduce the same at least 10° below its normal pour point. Depending upon the viscosity of the oil, an amount equivalent to yield in the depressed oil at least .01% to .25% metallic soap, such as aluminum stearate, will usually suffice. It is generally preferred, however, to procure maximum depression of pour point for a given oil and, in most cases, depending upon the viscosity of the oil, approximately .1% to .5% metallic soap such as aluminum stearate will produce such result.

In the following Table I a series of pour point reversion tests are tabulated for an SAE 10 and an SAE 40 oil respectively. In both cases the oil depressed with aluminum stearate alone showed an absolute reversion after 168 hours, in one case of 60° and in the other case of 35°, whereas in both instances the reversion of the pour point of the oil containing sodium mahogany sulphonate was zero.

Table I

	Reversion depressed pour point ° F.	Pour point ° F. after—			
		24 hrs.	48 hrs.	72 hrs.	168 hrs.
S. A. E. 10 Penn. grade oil original pour point +25° F.:					
Aluminum stearate alone.	-30	-25	-10	0	+25
Aluminum stearate + sodium mahogany sulphonate.	-30	-30	-30	-30	-25
S. A. E. 40 Penn. grade oil original pour point +25° F.:					
Aluminum stearate.	-10	-5	0	+10	+25
Aluminum stearate + sodium mahogany sulphonate.	-10	-10	-10	-10	-10

The pour point measurements of the untreated oil were carried out as prescribed by the well known ASTM test for the determination of pour point, designated as D97-39. The revision data recited in the foregoing table were obtained by storing the oil at 32° F. and observing the temperature at which the oil loses fluidity after the indicated time intervals.

The metallic soap-petroleum sulphonate depressant in accordance with the invention may be added to the waxy hydrocarbon oil, the pour point of which is to be depressed either as such, i. e., in substantially dry form, or in the form of a concentrated base in a suitable carrier. The latter method is conventionally practiced in connection with the use of pour point depressants generally and offers certain advantages such as ease of handling and of distribution in the oil

to which the depressant is to be added. Though a variety of organic liquids may be used as a carrier, it is as a rule preferred to select as the carrier a suitable hydrocarbon oil and preferably a hydrocarbon oil of the lubricating oil distillate range. When adding the metallic soap-sulphonate depressant in substantially dry form to the waxy hydrocarbon oil, it is preferred to accomplish the addition while the oil is hot.

The preparation of a metallic soap depressant base or concentrate has in the past offered a variety of disadvantages, foremost among which has been the occurrence of gel formation in the base as the consequence of peptization resulting in the partial or total loss of homogeneity of the base when comparatively large amounts of soap are present. For the purpose of preserving at least some degree of homogeneity it has been hitherto necessary to materially reduce the metallic soap concentration of the base and even then peptization of the gels formed upon storage results in the formation of a precipitate of substantially undissolved discrete soap particles. When preparing a depressant, however, in accordance with the invention, i. e., a depressant containing, in addition to the metallic soap or mixture of metallic soaps, a suitable oil soluble petroleum sulphonate, the afore-described disadvantages are substantially eliminated and the base or concentrate, substantially comprising a solution of the metallic soap-sulphonate depressant is substantially free from gel formation. The gel formation in the base or concentrate is to such an extent suppressed that, whereas in the past a maximum of but approximately three to four percent of a metallic soap, such as aluminum stearate, was capable of solution by the hydrocarbon oil carrier, and only then with the aid of a suitable gel breaking material, it is now possible to dissolve in the presence of the oil soluble petroleum sulphonate as high as 48% and sometimes even higher amounts of a suitable metallic soap in the hydrocarbon oil carrier. Thus the production of a pour point depressant base or concentrate is possible which is approximately twelve times as powerful as could hitherto be obtained.

When using the metallic soap-petroleum sulphonate depressant in accordance with the invention in the form of a base, it is desirable that the volume of the hydrocarbon oil carrier is such that it is at least sufficient to wet the entire amount of oil soluble metallic soap, such as a metal stearate, and dissolve the oil soluble petroleum sulphonate. Approximately 30% of oil carrier will suffice in most cases for this purpose. In many instances it is of advantage to use as the carrier that petroleum hydrocarbon oil to which the base or concentrate containing the depressant is to be added for the purpose of reducing its pour point. When using as the petroleum sulphonate component of the base a mixture of sulphonates obtained from the acid treatment of a lubricating oil distillate under sulphonating conditions as before described and containing retained oil, the latter may serve as the carrier, thus eliminating the necessity for further hydrocarbon oil addition to the base. In the majority of cases it is preferred to use in excess of 30% and preferably between 45 and 94% petroleum hydrocarbon oil carrier (by weight) for the base.

The oil soluble metal soap should be present in the hydrocarbon oil carrier to an appreciable extent, and preferably at least in, or in excess of, normally gel forming amounts (i. e., at least, or in

excess of, 4% stearate). The concentration of stearate in the oil carrier may, however, range from as low as 1% to as high as 48%. In most cases, depending upon the amount and type of oil soluble metallic soap used in the base, amounts of between 2% and 15% of oil soluble petroleum sulphonate content are recommended for the base.

Where in the specification and claims reference is made to the term "solution" in connection with a petroleum hydrocarbon oil carrier and its content of oil soluble metal stearate and oil soluble metal petroleum sulphonate, or where such stearate and sulphonate are designated as being "dissolved" in such oil carrier, it is intended that such term or designation or any expression of similar import generically connote not only true solutions but also colloidal or semi-colloidal dispersions.

Once the base or concentrate is prepared the same may be stored or shipped and used as required and will remain substantially fluid and non-gel forming in storage.

When a base or concentrate prepared in accordance with the invention contains approximately 4% aluminum stearate, 2% sodium mahogany sulphonate and 94% carrier oil, of which 0.6-0.7% is retained oil, an addition of approximately 3% of this base or concentrate to a Pennsylvania paraffin base oil will yield therein a stearate content of approximately 0.12% and a sulphonate content of approximately 0.04%.

The following Tables II and III illustrate the pour point reduction of various Pennsylvania paraffin base oils after the addition of the metallic soap-petroleum sulphonate depressant in accordance with the invention. Whereas Table II shows various paraffin base oils of substantially the same stearate and sulphonate content, i. e., approximately .12% aluminum stearate and .04% sodium mahogany sulphonate, Table III illustrates various Pennsylvania paraffin base oils of differing stearate and mahogany sulphonate content, the minimum absolute depression of the pour point of each oil being 10°.

Table II

Pennsylvania paraffin base oil (containing .12% Al stearate-.06% NaMah. sulphonate)	Normal pour point	Reduced pour point	Absolute depression
	°F.	°F.	
S. A. E. 10.....	-25	-30	55
S. A. E. 20.....	-25	-20	45
S. A. E. 30.....	-25	-10	35
S. A. E. 40.....	-25	-10	35
S. A. E. 50.....	-25	0	25

Table III

Al stearate	NaMah. sulphonate	Pennsylvania paraffin base oil				
		S. A. E. 10	S. A. E. 20	S. A. E. 30	S. A. E. 40	S. A. E. 50
			Depression pour point			
.25.....	.08.....	55	45	40	35	20
.18.....	.06.....	55	40	35	25	10
.12.....	.04.....	50	35	25	10	
.06.....	.02.....	30	25	10		
.03.....	.01.....	25	10			
.01.....	.003.....	10				

The depressed pour point obtained in each of the oils listed in Tables II and III was free from reversion as compared with the pour point of the same oils containing the same aluminum stearate content but without the addition of the ma-

hogany sulphonate which progressively reverted to normal.

The foregoing description is for purposes of illustration and not of limitation, and is not to be limited except by the appended claims in which I have endeavored to claim broadly all inherent novelty.

I claim:

1. A lubricating oil composition of relatively low, substantially non-fugitive, non-reverting pour point comprising a wax-containing petroleum hydrocarbon oil having normally a relatively high pour point due to the wax contained therein, a polyvalent metal stearates pour point depressant in amount and potency sufficient to lower said pour point and an oil soluble metallic petroleum sulphonate, said sulphonate and said soap being present in a ratio of 1:10 to 1:2.

2. A lubricating oil composition of relatively low, substantially non-fugitive, non-reverting pour point comprising a wax-containing petroleum hydrocarbon oil having normally a relatively high pour point due to the wax contained therein, approximately .01 to .5% polyvalent metal stearates pour point depressant for such oil and approximately .001 to .25% oil soluble metallic petroleum sulphonate.

3. A lubricating oil composition of relatively low, substantially non-fugitive, non-reverting pour point comprising a wax-containing petroleum hydrocarbon oil having normally a relatively high pour point due to the wax contained therein, approximately .1 to .25% polyvalent metal stearates pour point depressant for such oil and approximately .01 to .125% oil soluble metallic petroleum sulphonate.

4. A lubricating oil composition in accordance with claim 3 in which said metallic soap depressant is aluminum stearate and in which said oil soluble petroleum sulphonate is alkali petroleum mahogany sulphonate.

5. A lubricating oil composition in accordance with claim 3 in which said metallic soap depressant is aluminum stearate and in which said oil soluble petroleum sulphonate is tin petroleum mahogany sulphonate.

6. A lubricating oil composition comprising a wax-containing petroleum hydrocarbon oil of normally high pour point and small quantities of at least one soap having pour point depressing properties selected from the group consisting of polyvalent metal stearates, and palmitates, and an oil soluble metallic petroleum sulphonate, said soap being present in amount and potency sufficient to lower said pour point at least 10° F.

7. A lubricating oil composition comprising a wax-containing petroleum hydrocarbon oil of normally high pour point and small quantities of aluminum stearate in amount and potency sufficient to lower said pour point at least 10° F. and an oil soluble metallic petroleum sulphonate.

8. A lubricating oil composition of relatively low, substantially non-fugitive, non-reverting pour point comprising a wax-containing petroleum hydrocarbon oil, having normally a relatively high pour point due to the wax contained therein, a metallic soap pour point depressant composed of at least one member selected from the group consisting of polyvalent metal stearates and palmitates in amount and potency sufficient to lower said pour point at least 10° F., and an oil soluble metallic petroleum sulphonate, said sulphonate and said soap being present in a ratio of at least 1:10.

ISADOR SILVERMAN.