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 steatates, have in the past been used for 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-called "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 components independent 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 gener-

ically any one or more oil soluble metal salts of a sulphonated hydrocarbon or mixture of hy-

drocarnons 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 there-
to 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. Depend-
ing upon the viscosity of the oil, an amount equivalent to yield in the depressed oil at least .01% to .28% metallic soap, such as alumi-
nium stearate, will usually suffice. It is gener-

ally preferred, however, to procure maximum de-

pression 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 alpha-

num 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 188 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>
<thead>
<tr>
<th>Reversion depressant</th>
<th>Pour point ° F. after—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hrs.</td>
</tr>
<tr>
<td>S. A. E. 10 Penn. grade oil original pour point 45° F.:</td>
<td></td>
</tr>
<tr>
<td>Aluminum stearate alone.</td>
<td>-30</td>
</tr>
<tr>
<td>Aluminum stearate + sodium mahogany sulphonate.</td>
<td>-30</td>
</tr>
<tr>
<td>S. A. E. 40 Penn. grade oil original pour point 42° F.:</td>
<td></td>
</tr>
<tr>
<td>Aluminum stearate.</td>
<td>-10</td>
</tr>
<tr>
<td>Aluminum stearate + sodium mahogany sulphonate.</td>
<td>-10</td>
</tr>
</tbody>
</table>

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 tem-

perature at which the oil loses fluidity after the

indicated time intervals.

The metallic soap-petroleum sulphonate de-

pressant 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 con-

nection 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 car-

rier, it is as a rule preferred to select as the car-

rier a suitable hydrocarbon oil and preferably

a hydrocarbon oil of the lubricating oil distillate

range. When adding the metallic soap-sulpho-

nate depressant in substantially dry form to the

waxy hydrocarbon oil, it is preferred to accom-

plish the addition while the oil is hot.

The preparation of a metallic soap depressant
base or concentrate has in the past offered a vari-

ey 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 peptiza-
tion of the gels formed upon storage results in

the formation of a precipitate of substantially

undissolved discrete soap particles. When pre-

paring a depressant, however, in accordance with

the invention, i.e., a depressant concentrate, in

addition to the metallic soap or mixture of met-

talic soaps, a suitable oil soluble petroleum sul-

phonate, the afore-described disadvantages are

substantially eliminated and the base or concen-

trate, substantially comprising a solution of the

metallic soap-sulphonate depressant is substi-

tially 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 carri-

er, 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 sul-

phonate as high as 45% and sometimes even

higher amounts of a suitable metallic soap in the

hydrocarbon oil carrier. Thus the produc-

tion of a pour point depressant base or concen-

trate is possible which is approximately twelve
times as powerful as could hitherto be obtained.

When using the metallic soap-petroleum sul-

phonate depressant in accordance with the inven-
tion, in 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 pet-

roleum 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 re-

ducing its pour point. When using as the pet-

roleum sulphonate component of the base a mix-
ture of sulphonates obtained from the acid treat-

ment of a lubricating oil distillate under sulphon-

ating conditions as before described and con-

taining retained oil, the latter may serve as the

carrier, thus eliminating the necessity for fur-

ther hydrocarbon oil addition to the base. In

the majority of cases it is preferred to use in ex-
cess 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
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 "sulphonation" 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 5% 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 Pennsylvania 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

<table>
<thead>
<tr>
<th>Oil</th>
<th>Stearate %</th>
<th>Sulphonate %</th>
<th>Pour Point Depression</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. A. E. 10</td>
<td>0.06</td>
<td>0.005</td>
<td>25</td>
</tr>
<tr>
<td>S. A. E. 20</td>
<td>0.12</td>
<td>0.01</td>
<td>20</td>
</tr>
<tr>
<td>S. A. E. 30</td>
<td>0.18</td>
<td>0.015</td>
<td>15</td>
</tr>
<tr>
<td>S. A. E. 40</td>
<td>0.24</td>
<td>0.02</td>
<td>10</td>
</tr>
</tbody>
</table>

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 metal 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 stearate 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 metallic stearates pour point depressant for such oil and approximately .001 to .005% 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 metallic stearates pour point depressant for such oil and approximately .01 to .15% 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 metal 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 metal 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.