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POUR POINT DEPRESSANT OF HIGH STRENGTH AND PROCESS FOR PREPARING SAME

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The present invention relates to improvement of lubricating oils and more specifically to improved means for producing low pour point oil from wax-containing fractions of high pour point. The present invention will be fully understood from the following description.

It has been previously disclosed that the addition of certain substances to wax-containing oils of high pour point greatly improves these oils causing them to have a much lower congealing point on cooling. Previously the customary manner of producing low pour point oils was to secure a crude in which no wax occurred or if a waxy crude was used to freeze the oil and remove the solid constituents by cold settling, filtration or centrifugal means. All of the methods for producing these low cold test oils from high grade paraffin base crudes involve refrigeration which entails relatively high costs especially when the pour point is to be reduced below zero degrees Fahrenheit.

Very satisfactory types of pour point depressants have been produced by the low temperature aluminum chloride condensation of waxy hydrocarbons with or without an aromatic hydrocarbon such as naphthalene. The condensation products of waxy hydrocarbons with aromatic hydrocarbons have been described in U. S. Patent 1,815,022. Such a synthetic material is added in proportion of the order of 1% of the wax containing oil.

It was previously supposed that the condensation product was of more or less uniform composition, at least in regard to its pour inhibiting properties, but it has been found that this is not the case and that the synthetic material is a mixture of three classes of substances which are quite different.

It has been found that the lighter fractions boiling up to say 650 or 700° F. possess little or no pour depressant properties: furthermore, it has been determined that the remaining material is composed of an inactive waxy material with a molecular weight below about 1000 or 1200 and viscous liquid or semi-solid hydrocarbons of higher molecular weight which have extremely powerful pour depressant properties.

It has now been found that the most effective portion of this class of hydrocarbon inhibitors can be readily concentrated and by this means oils of greatly lower pour point can be made, or on the other hand the pour point of a given oil may be depressed to the same extent by the use of greatly reduced quantities of the inhibitor.

In the practice of this invention it will be understood that the crude inhibitor is made for example by the condensation of a waxy hydrocarbon with or without aromatic hydrocarbons such as naphthalene. Condensation is preferably brought about by first chlorinating paraffin wax and then condensing it in a kerosene medium by means of aluminum chloride or its well known equivalents such as zinc chloride. The temperature of chlorination is preferably 200 to 350° F. and that of condensation is preferably about 70 to 150° F. Condensation takes place within about 24 hours. The aluminous sludge is separated at the end of this time, the oil is removed and then distilled to remove the kerosene and preferably a part of the wax. This distillation may be carried out under vacuum so as to avoid any cracking. The following inspections may be given as characteristic of the type of product produced by the foregoing steps, although it will be understood that it may vary considerably depending on the extent of chlorination, proportions of chlorinated paraffin to naphthalene, the duration of the heating and the temperature of condensation.

	Sample I	Sample II
Gravity	23.4° A. P. I.	22.0° A. P. I.
Vis. @ 100° F.	8500 sec. Saybolt	4960 sec.
Vis. @ 210° F.	312 sec. Saybolt	289 sec.
Pour point	65° F.	45° F.

This material or its equivalent, which is produced as indicated above, will be designated as crude inhibitor and according to the present invention it is subjected to the purification steps disclosed below.

The method of concentration which is most satisfactory is that of solvent-extraction, and as solvents the class of organic substances generally known as wax precipitants may be used. As will be understood they do not have a high solubility for wax or rather the solubility drops off more rapidly with decreasing temperature in such materials than in the petroleum medium in which the wax naturally occurs.

These wax precipitants are generally miscible with gas oil and the lighter lubricating fractions at room temperatures or at slightly elevated temperatures, but as temperature is reduced the wax is caused to precipitate. Now it has been found that in spite of the relatively poor solubility of such substances for wax they are even poorer solvents for the heaviest fractions of the crude inhibitor which is the portion richest in fractions

possessing pour-depressant properties. In general the class of wax precipitants includes light hydrocarbons, alcohols, esters, ketones, organic acids, alkyl halides such as ethylene dichloride, carbon tetrachloride, phenols, aniline, furfural, liquid sulphur dioxide and the like. Among the light hydrocarbons propane or preferably mixtures of butane, propane and ethane or any two of these are satisfactory. Amyl alcohols, butyl alcohols or their mixtures or ethyl or methyl or propyl alcohols or their mixtures with each other or with higher alcohols, or kerosene and amyl alcohol, or, better pentane and amyl or butyl alcohol may be used as solvents but it is understood that these are merely illustrations and that any of the single substances or mixtures from the class of wax precipitants may be used.

Different solvents may be used successively or the same solvents may be used in successive fractions. It will be understood that the solvent is used in rather large proportions for example 8 or 10 parts of solvent to 1 of the crude inhibitor, when it is desired to separate the wax from the less miscible heavy oil fractions. The exact composition of the mixed solvent should be left to trial since slight differences in the crude or original inhibitor frequently occur. Likewise the temperature of extraction may be adjusted to give the cleanest and most effective separation. Ordinarily the solvent compositions may be adjusted so that the separation occurs at about room temperature but in some cases it is better to cool during the extraction.

There are two general methods by which the separation may be accomplished. By the first method small amounts of a wax precipitant may be used to precipitate a mixture of wax and an active heavy end from the lighter oil. As will be understood this precipitated mixture will contain more wax than the original oil. The precipitate is removed by settling, filtration or centrifugal means and the solid wax is extracted from the oil by solution in a larger quantity of the same or other solvent. In the first step the solvent separates with the lighter oil and precipitates the wax and heavy oil fractions. In the second step the solvent acts as a true solvent for wax and dissolves it out, but does not mix with the liquid heavy ends which possess powerful depressant properties. The liquid layers are drawn off separately.

In the second method large amounts of solvents may be used immediately so as to dissolve both the light ends and the soluble wax. In this method the lighter oil fraction is apt to occlude or dissolve a higher proportion of the heavy active product, and it may be subjected to a further extraction.

One series of steps is especially desirable. The crude inhibitor is mixed with amyl alcohol or its equivalent precipitant. The solid mass thus precipitated is then removed and extracted with pentane or say a mixture of pentane and amyl alcohol, which is a fairly good solvent for wax, but which is not miscible with the active heavy ends.

The following examples may be given as illustrative of the solvents and the conditions required:

1. The crude product is extracted three successive times with about 3 volumes of a solvent composed of one part of kerosene and 12 parts of secondary amyl alcohol. The extraction is carried out at room temperature and the undissolved portion comprises 15% of the original. The extracted oil (85%) shows little or no pour reducing properties but the undissolved 15% is some 6 or 7 times as powerful as the original. The pour point of a Bayonne engine oil with a normal pour point of 30° F. is reduced by the concentrate by some 20° F. more than by an equal quantity of the crude inhibitor. In other tests it is found that .15% of the concentrate is as effective as 1% of the original.

2. The crude inhibitor is carefully distilled and about 30% of a waxy practically inactive product is taken overhead as distillate. The temperature is carefully controlled at a point below which cracking commences. The 70% residue, which is in itself notably better than the original as a pour depressant, is then extracted with four successive portions of the same solvent used in Example 1 using three volumes of solvent for each volume of oil to be extracted, and a concentrate comprising 15% of the original is recovered free from wax and substantially as active as the concentrate obtained in Example 1.

3. The crude inhibitor, 1% of which is capable of reducing the pour point of an engine oil from 30° to 10° F. is dissolved in 10 volumes of a solvent comprising substantially pure propane. The mixture is reduced in temperature to —45° F. and two layers are obtained. The upper one comprising 40% of the original failed to show any effect on the pour point of the engine oil mentioned in Example 1, while 1% of the second fraction, comprising 60% of the original showed an increased reduction of the pour point of the engine oil.

4. The crude inhibitor is mixed with the solvent comprising 75% propane and 25% ethane in proportion of 10 volumes of solvent to one of oil. Two fractions are obtained at room temperature, the one, comprising 65%, reduces the pour point of the engine oil referred to in Example 3 to 25° F. when 1% is used. The second fraction comprising 35% of the original reduces the pour point of the same oil to —5° F. when used in the same proportion.

5. The 35% fraction obtained in Example 4 is re-extracted as before with the same solvent. The upper layer obtained by this second extraction and comprising 13% of the original when used in 1% proportion reduces the pour point of the engine oil from 30° to 25° F. and is therefore only slightly active. The second fraction comprising 22% of the orginal inhibitor reduces the pour point to —20° F. when used in 1% proportion.

6. Using 10 volumes of a solvent comprising 25% ethane and 75% propane, the crude condensation product is separated into a soluble portion 44%. The remaining 56% is extracted again with another batch of the same solvent and 13% is removed. A third extraction removes 5% leaving 38% of the original which is very active.

The 38% remaining is then extracted with 10 volumes of a solvent comprising 50% propane and 50% butane. 7.5% based on the original is undissolved and is found to be very powerful.

Percent in a 30° pour point oil	Original inhibitor	7.5% concentrate
1 percent	—10° F.	
½ percent	+5° F.	—30° F.
1/16 percent		0° F.

The above table indicates the high concentration obtained.

When using solvent mixtures, such as ethane or propane or in fact any mixed solvents the proportion of the constituents is very important. For example, the composition of 75% propane and 25% ethane is effective at about room temperature. When using 85% propane and 15% ethane no separation is obtained. The proper composition depends on a number of factors which may be determined by simple tests. As a rule it is desirable to make several successive extractions with solvent of increasing solvent power, for example using increasingly greater proportion of propane or butane to ethane as the fraction to be extracted becomes richer in the active ingredients and correspondingly poorer in inactive motor oils.

The concentrated material obtained by these extraction processes is an oily viscous liquid or semi-solid product substantially free from wax and while it varies somewhat according to the conditions of manufacture of the original inhibitor and of the method of extraction the following may be taken as typical:

Gravity	18.5° A. P. I.
Vis. @ 210	2278 sec. Saybolt
Pour point	65° F.

The concentrated material has a molecular weight in excess of about 1200 when determined by the effect on the melting point of camphor, the pour inhibiting effect of the concentrated material is much greater than the original. This has been shown in the examples above but additional illustrations follow: 1% of a particular original inhibitor reduced the pour point of a wax containing oil from 30° F. to 0° and 6% of the inhibitor reduced it to −15° F. In higher concentrations there is substantially no further effect on the pour point. The concentrate from this particular crude inhibitor obtained by the methods given above and which comprises 20 to 25% of the total when used in a proportion of ¼ of 1% reduced the pour point of the distillate referred to above 0° F. ½ of 1% reduced it to −15° F. while in 1% concentration the pour point is reduced to −20° F. It was impossible to produce a pour point of −20° F. with the original material in whatever quantity it was used. It will be understood that different batches of the crude inhibitor differ somewhat in their quality as pour depressants and also they are somewhat more effective in certain oils such as hydrogenated oils, but in all cases observed, the concentration effects a marked improvement.

It should be understood that the reduction in pour point is permanent and stable and that the blended oil is substantially the equal of an unblended oil in respect to gravity, viscosity, viscosity index, demulsibility, flash and fire points and resistance both to oxidation and corrosion. The color is slightly lowered and Conradson carbon somewhat increased but not to a serious extent. The lighter fractions while not useful as pour inhibitors are excellent lubricating oils of the lighter grade. They may be used as spindle or motor oils either alone or suitably blended with petroleum fractions. The following inspection of the lighter inactive portion obtained in Example 3 is characteristic:

Gravity	25.8° A. P. I.	
Vis. @ 100° F.	1446	sec. Saybolt
Vis. @ 212° F.	127	sec. Saybolt

The wax is also of a high quality similar to paraffin wax occurring naturally except that it has a much higher molecular weight 800 for example, and a higher melting point.

The prior description has been based mainly on concentration of active ingredients in a condensation product of chlorinated paraffin wax and naphthalene but it is applicable to other valuable hydrocarbon pour inhibitors produced by condensation of waxy hydrocarbons, that is, through their active derivatives such as olefins, halides and the like either with or without aromatic hydrocarbons. It will be understood that by the term "active derivatives of waxy hydrocarbons" is meant hydrocarbons having substantially the original wax skeleton which have been partially unsaturated by dehydrogenation, halogenation and splitting off of hydrogen halide or other methods that do not involve breaking of the hydrocarbon chain. This term therefore excludes derivatives obtained by cracking waxy hydrocarbons because cracking results in a substantial rupturing of the original wax skeleton. The conditions for polymerization and concentration may be substantially the same in all cases as given above.

The process is not to be limited to any theory of the mechanism of the extraction process nor to any particular solvent or solvent mixtures but only by the following claims in which I wish to claim the invention as broadly as the prior art permits.

I claim:

1. An improved process for separating highly active substances for depressing the pour point of waxy lubricating oils from a crude depressor obtained by low temperature aluminum chloride condensation of waxy hydrocarbons, comprising separating inactive materials from the crude depressor by extraction in a solvent of the class of wax precipitants.

2. An improved process for producing highly active substances for depressing the pour points of lubricating oils comprising segregating from a crude hydrocarbon inhibitor derived by low temperature aluminum chloride condensation of active derivatives of waxy hydrocarbons in absence of aromatics, a heavy fraction by careful distillation of lighter inactive fractions at temperatures to avoid decomposition, and then extracting further inactive materials from the residue with a relatively large portion of a solvent from the class of waxy precipitants.

3. An improved process for separating highly active substances for depressing the pour point of waxy lubricating oils from a crude depressor obtained by low temperature aluminum chloride condensation of waxy hydrocarbons, comprising separating inactive materials from the crude depressor by extraction in a solvent of the class of wax precipitants selected from the group consisting of butyl alcohol and amyl alcohol.

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