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LUBRICATING OIL COMPOSITION

Franz Rudolf Moser, Amsterdam; Netherlands; vested in the Alien Property Custodian

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This invention deals with compounded mineral lubricating oils and, more particularly, deals with the addition of polyvalent metal salts of rosin oil or tall oil to mineral oils to produce lubricating oils of improved antigumming properties for internal combustion engines, which oils have the property of preventing the sticking of piston rings when running these engines for long periods of time, and which have the ability to properly lubricate the cylinders and pistons under severe conditions of loading, i. e. which prevent cylinder abrasion.

It is known that in modern engines, such as high speed Diesel engines, aviation gasoline engines, etc., which, due to their high power output, operate at relatively high temperatures, piston rings have a tendency to become stuck in the grooves. Lacquer and/or carbon formation appear to be the principal reasons for this occurrence. The addition of small amounts of certain oil-soluble carboxylic salts, such as polyvalent metal salts of fatty acids and other carboxylic acids, is known known to reduce the ring-sticking tendencies. Many of the salts are not readily soluble in the mineral oil and, therefore, may settle out under lubricating conditions. Moreover, certain of these salts cause gelatinization while others are relatively expensive.

Now, in accordance with my invention, I have found that the polyvalent metal salts of liquid rosin oil when added to mineral oil in suitable quantities produce effective anti-ring-sticking lubricants which are relatively free from the above disadvantages.

Rosin oils are by-products of the paper industry and may be obtained by treating the wood of coniferous trees by the sulfate process for wood pulp production. In this process the chipped wood is boiled with a sulfate solution, and the residual waste liquor is allowed to separate in two layers, the upper layer being the rosin oil. Considerable quantities of such rosin oils are produced in Sweden and are often referred to as talloils.

Rosin oils consist predominantly of mixtures of rosin acids and fatty acids in varying ratios and also contain small amounts of unsaponifiable materials. Different rosin oils contain different rosin acids, and the fatty acids may be unsaturated. The degree of unsaturation may be very high, and this may be the reason why some of the rosin oil salts cause gummy precipitates. Sludging and precipitation of many rosin oil salts may be reduced considerably by partially hydrogenating the rosin oils. If hydrogenation is carried too far, however, polyvalent metal salts of the resulting hydrogenated rosin oil may be difficultly soluble in hydrocarbon oils. Therefore, hydrogenation should be carried out to a degree only so as to yield a hydrogenated product, the polyvalent metal salts of which are at least about 2% soluble in mineral lubricating oils.

When subjecting rosin oils to fractional distillation, the first fractions coming over normally consist mainly of fatty acids, while the higher boiling fractions usually consist predominantly of rosin acids and unsaponifiable substances. The middle fractions are usually composed of mixtures of fatty acids and rosin acids and are particularly suitable for my purpose if they contain the two types of acids in approximately equal amounts. The presence in lubricating oils of the unsaponifiable substances naturally contained in rosin oils may often be harmful, and it is, therefore, often desirable to eliminate these substances from the rosin oil either by distillation or by other appropriate means.

It is also possible to use soaps of fractions of talloil, which fractions can be prepared in several ways (vacuum distillation, treatment with solvents, and the like).

Thus, in order to prevent the usual oxidation tests of the lubricating oil being adversely affected by the addition according to my invention, the talloil may be subjected to a refining treatment, by which the most readily oxidizable part is removed. This refining treatment may be a known treatment for oils and greases, e. g. a treatment with sulfuric acid.

The treatment with sulfuric acid may be carried out as follows:

A quantity of talloil distillate is taken up in an equal volume of gasoline, whereupon 5% by weight concentrated sulfuric acid is added while stirring, the temperature being maintained at about 25° C. After this treatment the acid tar is removed, whereupon 10% by weight terrana or adsorption agent is added, the gasoline is distilled off and the mixture of talloil and terrana is kept for some time at a temperature of 150° C., while steam or an inert gas is blow through it. After cooling the mixture is filtered; the refined talloil thus obtained has become appreciably lighter in colour.

I have found that for good solubility of the polyvalent metal salts in mineral lubricating oils, it is desirable that mixtures of fatty acids and rosin acids be employed in which the ratio of rosin acids to fatty acids is between the limits of about 4:1 and 1:4 and preferably about 1:1. This latter ratio of fatty acids to rosin acids is approximately that found in many of the rosin oils produced in Sweden.

In general, the rosin acids are far superior to fatty acids as ring-sticking inhibitors, whereas the fatty acids and, more particularly, unsaturated fatty acids tend to promote the solubility of the rosin acids in mineral lubricating oils. If a natural rosin oil is deficient in one or the other types of acid, it may be desirable to cure this deficiency by adding a suitable amount of that type of acid which is lacking. For example, I may utilize the lowest or higher boiling fractions, as the case may be, obtained in the fractional distillation of suitable rosin oils for blending back. Likewise, I may produce suitable blends of the lowest and higher boiling fractions, preferably selecting those of the higher boiling fractions which are substantially free from the unsaponifiable substances.

The rosin oil salts can be produced, for example, by double decomposition of rosin oil neutralized with lye and water-soluble salts of polyvalent metals. The desired salts are precipitated and then separated. Purified rosin oil salts may be obtained by extracting the precipitate, for instance, with ether or benzene in which they dissolve, whereupon they may be recovered by evaporating the solvent. Or else the rosin oil may be directly saponified with the oxide or hydroxide of the desired metal, preferably while stirring and heating to 100°C–200°C.; the occasional addition of a small quantity of water promotes the dissolution. It is advantageous to use an amount of the metal of the saponified agent in excess of the mol equivalent of the acids contained in the rosin oil, because in this manner basic rosin oil salts may be produced which are less corrosive than the normal salts.

The use of a more than equivalent quantity of metal oxide presents the advantage of reducing the corrosive properties of the soap, practically even to zero. If talloil soaps are produced from equivalent quantities of metal oxide and talloil, it has been found that mixtures of neutral soaps, basic soaps and free acids are obtained, the latter causing corrosiveness. These free acids may be removed by the use of a larger quantity of oxide; they may also be removed or rendered innocuous by other chemical or physical methods. The excess of oxide admissible in connection with the solubility of the soaps in lubricating oil can be readily determined by experiment in each case.

Of the polyvalent metals whose salts of rosin oil may be suitable for anti-ring sticking purposes, magnesium, calcium, strontium, barium, cadmium, zinc, nickel, cobalt, and aluminum seem to be most active. Especially effective are the rosin oil salts of magnesium, calcium and zinc.

Although I prefer to use about .5 to 2% of the rosin oil salts in my lubricating oil, amounts may be varied from approximately .2 to 5%. Amounts in excess of the 2% limit may cause undue increase in viscosity, jelling of the oil, and a tendency to cause substantially permanent emulsions. The tendency toward emulsification varies with different metals in the salt. For example, the zinc salts do not cause permanent emulsions when used in amounts up to 5%, particularly if they are well purified, as by extraction or fractional distillation of the talloil. In the following table data are presented showing the effectiveness of different concentrations of the zinc salts of rosin oil as anti-ring-sticking agents in a medium grade mineral lubricating oil in a Deutz gasoline engine. The tests were made at 1200 RPM and were of 12 hour duration, while maintaining a jacket temperature of about 200° C.

Table

Concentration of rosin oil-zinc salt	Ring-sticking [1,2]	Formation of carbon on the inside of the bottom of the piston [1]	Formation of carbon in the ring grooves [1]
Percent		*Grams*	*Grams*
2	0.0	0.35	0.34
1	0.0	1.03	0.51
0.5	0.2	1.53	0.84
None	1.0	2.34	1.29

[1] Average values of a number of experiments.
[2] 1.0=one ring completely stuck all the way around; the values of the four rings were totalled.

Crankcase lubricating oils containing salts of rosin oil may also contain other compounding ingredients, such as oxidation inhibitors, anti-corrosion agents, other soaps, pour-point depressors, blooming agents and extreme pressure agents, preferably those containing at least one of the elements of phosphorus, sulfur, or chlorine.

The following examples further illustrate our invention:

Example I

About 1% by weight of a zinc salt of "Swedish" tall oil was added at 100°C to a Venezuelan lubricating oil distillate (aviation grade lubricating oil) refined with furfural. The resulting lubricating oil was found to be suitable for internal lubrication of Diesel engines, materially retarding ring-sticking. Upon use no sediment was formed and the oil gave no rise to gum formation.

Example II

A crude talloil is distilled in vacuo with steam until about 85% distillate has been obtained. First runnings of about 15% are not used, because they contain substances that would impart a disagreeable odour to the final product. Zinc oxide, in a 25% excess calculated on the normal soap, is added, while stirring, to the distillate (acid figure 162) consisting of approximately equal parts of resinic acids and fatty acids. The dissolution of the zinc oxide, which is continued until a clear solution has been obtained, is effected by heating up to about 200°C. From time to time some water is added in order to promote the dissolution. If 1 to 2% by weight of the product obtained is added to a lubricating oil, ringsticking and carbon deposition are avoided and no corrosiveness is found.

Example III

10% sodium hydroxide solution is added to a talloil distillate according to Example II in a 100% excess—calculated on the acid figure of the talloil and then a magnesium chloride solution is added in a 100% excess.

The precipitate is washed by suspension in water and dried at 120°C. The product obtained has an ash content 38% higher than that of the normal salt; it is readily soluble in lubricating oil and does not impart any corrosive properties to it. Ring-sticking and carbon deposition are avoided by the addition of a quantity of 1 to 2% by weight of the said product to lubricating oil.

FRANZ RUDOLF MOSER.