

Description

The present invention relates to a method for reducing piston deposits in an internal combustion engine by using a soluble ashless detergent and a heterogenous strong base immobilized within the lubricating system of the engine.

The optimum functioning of an internal combustion engine (especially a diesel engine) requires that fuel combustion acids (e.g., carboxylic, nitric, nitrous, sulfuric and sulfurous acids -- with or without alkyl groups) be neutralized where they first contact the lubricant, i.e., at the piston. In the absence of this acid neutralization, the lubricant gels, its viscosity rapidly increases, and engine deposits are formed. This results in increased oil consumption and engine wear.

Traditionally metal-containing (i.e. ashcontaining) detergents (e.g., barium, calcium, or magnesium over-based sulfonates or phenates) have been used to neutralize combustion acids (See, for example, U.S. Patents 2,316,080; 2,617,049; 2,647,889; and 2,835,688). In the absence of metal detergents, as for example in ashless oils, polyethyleneamine based dispersants have been used for neutralization (See, for example, U.S. Patent 3,172,892). However, ashless detergents are generally not used in lubricating oils because polyethyleneamines are less cost effective than ash-containing detergents and normally do not maintain adequate TBN (Total Base Number).

Well formulated lubricants containing metal detergents are very effective in reducing piston deposits. Often, however, a limit is reached where it becomes increasingly more difficult to further reduce piston deposits. As this limit is approached, an appreciable percentage of piston deposits results from the metal component of the detergents. For example, the deposits on some pistons contain up to 34 wt.% calcium and magnesium. (See A. Sohetelich et al., "The Control of Piston Crown Land Deposits in Diesel Engines Through Oil Formulation," Soc. Automat. Eng. Tech., Pub. Ser. 861517 (1986)). Therefore, it would be desirable to have available a simple and convenient, yet cost effective, method for reducing piston deposits in an internal combustion engine and, preferably, for transferring or moving the deposits to a part of the engine's lubrication system where they will not impair engine performance.

This invention relates to a method for reducing piston deposits resulting from the neutralization of fuel combustion acids in the piston ring zone (i.e., that area of the piston liner traversed by the reciprocating piston) of an internal combustion engine. More specifically, these deposits can be reduced or eliminated from the engine by contacting the combustion acids at the piston ring zone with a soluble weak base for a period of time sufficient to neutralize a major portion (preferably essentially all) of the combustion acids and form soluble neutral salts which contain a weak base and a strong combustion acid. These soluble neutral salts then pass (or circulate) with the lubricating oil from the piston ring zone to a heterogenous strong base immobilized within the lubrication system of the engine. By "heterogenous strong base" is meant that the strong base is in a separate phase (or substantially in a separate phase) from the lubricating oil, i.e., the strong base is insoluble or substantially insoluble in the oil. When the neutral salts contact the strong base, the strong base displaces the weak base and releases it into the oil for recirculation to (and reuse in) the piston ring zone. The strong combustion acid/strong base salts formed from reacting the neutral salts with the strong base are immobilized as deposits on the heterogenous strong base and are, thus, removed from the oil, but at a location other than the piston ring zone. Preferably, the weak base is a trialkyl amine (e.g., trioctadecyl amine) and the strong base is zinc oxide. Most preferably the strong base will be incorporated on or with a substrate immobilized within the lubrication system, but outside of the piston ring zone.

Other embodiments of this invention include (1) a method for selectively transferring deposits (especially piston deposits) from one location in the lubrication system of an internal combustion engine to another location in the lubrication system by specifying the acid/base chemistry at each location and (2) a system for reducing deposits (especially piston deposits) in an internal combustion engine that utilizes a lubricating oil, a soluble weak base, and a heterogenous strong base to neutralize combustion acids and prevent the deposits from forming.

Figure 1 shows the change in Total Base Number with time for two lubricating oil blends.

Figure 2 shows the change in Total Acid Number with time for four lubricating oil blends.

Figure 3 shows the change in metal wear with time for four lubricating oil blends.

Figure 4 shows the change in percent pentane insolubles with time for four lubricating oil blends.

The lubricating (or crankcase) oil circulating within the lubrication system of an internal combustion engine will comprise a major amount of a lubricating oil basestock (or base oil) and a minor amount of one or more additives. The lubricating oil basestock can be derived from natural lubricating oils, synthetic lubricating oils, or mixtures thereof. In general, the lubricating oil basestock will have a viscosity in the range of 5 to 10,000 10^{-6} m²/S (cSt) at 40°C, although typical applications will require an oil having a viscosity ranging from 10 to 1,000 10^{-6} m²/S (cSt) at 40°C.

Natural lubricating oils include animal, vegetable (e.g., castor oil and lard oil), petroleum, or mineral oils.

Synthetic lubricating oils include alkylene oxide polymers, interpolymers, and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof (for example, the acetic acid esters, mixed C_3 - C_8 fatty acid esters, and C_{13} oxo acid diester of tetraethylene glycol).

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, dilauryl azelate, dioctyl phthalate, didodecyl phthalate, diicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricating oils; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxyl) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid); polymeric tetrahydrofurans, and polyalphaolefins.

The lubricating oil used may be derived from unrefined, refined, and rerefined oils. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The lubricating oil will contain a weak base, which will normally be added to the lubricating oil during its formulation or manufacture. Broadly speaking, the weak bases can be basic organophosphorus compounds, basic organonitrogen compounds, or mixtures thereof, with basic organonitrogen compounds being preferred. Families of basic organophosphorus and organonitrogen compounds include aromatic compounds, aliphatic compounds, cycloaliphatic compounds, or mixtures thereof. Examples of basic organonitrogen compounds include, but are not limited to, pyridines; anilines; piperazines; morpholines; alkyl, dialkyl, and trialkyl amines; alkyl polyamines; and alkyl and aryl guanidines. Alkyl, dialkyl, and trialkyl phosphines are examples of basic organophosphorus compounds.

Examples of particularly effective weak bases are the dialkyl amines (R_2HN), trialkyl amines (R_3N), dialkyl phosphines (R_2HP), and trialkyl phosphines (R_3P), where R is an alkyl group, H is hydrogen, N is nitrogen, and P is phosphorus. All of the alkyl groups in the amine or phosphine need not have the same chain length. The alkyl group should be substantially saturated and from 1 to 22 carbons in length. For the di- and tri- alkyl phosphines and the di- and trialkyl amines, the total number of carbon atoms in the alkyl groups should be from 12 to 66. Preferably, the individual alkyl group will be from 6 to 18, more preferably from 10 to 18, carbon atoms in length.

Trialkyl amines and trialkyl phosphines are preferred over the dialkyl amines and dialkyl phosphines. Examples of suitable dialkyl and trialkyl amines (or phosphines) include tributyl amine (or phosphine), dihexyl amine (or phosphine), decylethyl amine (or phosphine), trihexyl amine (or phosphine), trioctyl amine (or phosphine), trioctyldodecyl amine (or phosphine), tridecyl amine (or phosphine), dioctyl amine (or phosphine), triicosyl amine (or phosphine), tridocosyl amine (or phosphine), or mixtures thereof. Preferred trialkyl amines are trihexyl

amine, trioctadecyl amine, or mixtures thereof, with trioctadecyl amine being particularly preferred. Preferred trialkyl phosphines are trihexyl phosphine, trioctyldecyl phosphine, or mixtures thereof, with trioctadecyl phosphine being particularly preferred. Still another example of a suitable weak base is the polyethyleneamine imide of polybutenylsuccinic anhydride with more than 40 carbons in the polybutenyl group.

The weak base must be strong enough to neutralize the combustion acids (i.e., form a salt). Suitable weak bases will typically have a PKa from about 4 to about 12. However, even strong organic bases (such as organoguanidines) can be utilized as the weak base if the strong base is an appropriate oxide or hydroxide and is capable of releasing the weak base from the weak base/combustion acid salt.

The molecular weight of the weak base should be such that the protonated nitrogen compound retains its oil solubility. Thus, the weak base should have sufficient solubility so that the salt formed remains soluble in the oil and does not precipitate. Adding alkyl groups to the weak base is the preferred method to ensure its solubility.

The amount of weak base in the lubricating oil for contact at the piston ring zone will vary depending upon the amount of combustion acids present, the degree of neutralization desired, and the specific applications of the oil. In general, the amount need only be that which is effective or sufficient to neutralize at least a portion of the combustion acids present at the piston ring zone. Typically, the amount will range from about 0.01 to about 3 wt.% or more, preferably from about 0.1 to about 1.0 wt.%.

Following neutralization of the combustion acids, the neutral salts are passed or circulated from the piston ring zone with the lubricating oil and contacted with a heterogeneous strong base. By strong base is meant a base that will displace the weak base from the neutral salts and return the weak base to the oil for recirculation to the piston ring zone where the weak base is reused to neutralize combustion acids. Examples of suitable strong bases include, but are not limited to, barium oxide (BaO), calcium carbonate (CaCO_3), calcium oxide (CaO), calcium hydroxide (Ca(OH)_2), magnesium carbonate (MgCO_3), magnesium hydroxide (Mg(OH)_2), magnesium oxide (MgO), sodium aluminate (NaAlO_2), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), zinc oxide (ZnO), or their mixtures, with ZnO being particularly preferred.

The strong base may be incorporated (e.g., impregnated) on or with a substrate immobilized in the lubricating system of the engine, but subsequent to (or downstream of) the piston ring zone. Thus, the substrate can be located on the engine block or near the sump. Preferably, the substrate will be part of the filter system for filtering oil, although it could be separate therefrom. Suitable substrates include, but are not limited to, alumina, activated clay, cellulose, cement binder, silica-alumina, and activated carbon. The alumina, cement binder, and activated carbon are preferred, with cement binder being particularly preferred. The substrate may be inert or not inert.

The strong base may be incorporated on or with the substrate by methods known to those skilled in the art. For example, if the substrate were alumina, the strong base can be deposited by using the following technique. A highly porous alumina is selected. The porosity of the alumina is determined by weighing dried alumina and then immersing it in water. The alumina is removed from the water and the surface water removed by blowing with dry air. The alumina is then reweighed and compared to the dry alumina weight. The difference in weight is expressed as grams of water per gram of dry alumina. A saturated solution of calcium oxide in water is prepared. This solution is then added to the dry alumina in an amount equal to the difference between the weight of wet and dry alumina. The water is removed from the alumina with heat leaving CaO deposited on the alumina as the product. This preparation can be carried out at ambient conditions, except the water removal step is performed above 100°C .

The amount of strong base required will vary with the amount of weak base in the oil and the amount of combustion acids formed during engine operation. However, since the strong base is not being continuously regenerated for reuse as is the weak base (i.e., the alkyl amine), the amount of strong base must be at least equal to (and preferably be a multiple of) the equivalent weight of the weak base in the oil. Therefore, the amount of strong base should be from 1 to about 15 times, preferably from 1 to about 5 times, the equivalent weight of the weak base in the oil.

Once the weak base has been displaced from the soluble neutral salts, the strong base/strong combustion acid salts thus formed will be immobilized as heterogeneous deposits with the strong base or with the strong base on a substrate if one is used. Thus, deposits which would normally be formed in the piston ring zone are not formed until the soluble salts contact the strong base. Preferably, the strong base will be located such that it can be easily removed from the lubrication system (e.g., included as part of the oil filter system).

In addition to the weak base, other additives known in the art may be added to the lubricating base oil to form a fully formulated lubricating oil. Such lubricating oil additives include dispersants, antiwear agents, antioxidants, corrosion inhibitors, other detergents, pour point depressants, extreme pressure additives, viscosity index improvers, friction modifiers, and the like. These additives are typically disclosed, for example, in "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith, 1967, pp. 1-11 and in U.S. Patent 4,105,571. Nor-

mally, there is from about 2 to about 20 wt. % of these additives in a fully formulated engine lubricating oil.

Although this invention has been described heretofore with respect to reducing or eliminating piston zone deposits, the invention may be more broadly applied to reducing or eliminating deposits resulting from neutralizing essentially any acids present in the lubricating oil circulating with the lubrication system of essentially any internal combustion engine including gasoline, diesel, rotary, heavy feed, gas-fired, and methanol powered engines. This invention also does not contribute to particulate emissions in these applications because the need for ash-containing additives in the oil is reduced or eliminated.

In another embodiment, this invention is a method for causing (or transferring) deposits resulting from neutralizing acids present in the lubricating oil of an internal combustion engine (especially piston deposits), which deposits would normally form at one location in the lubrication system of the engine (e.g., the piston), to form in (or be transferred to) another location within the lubrication system (e.g., in the oil filter) by specifying the acid/base chemistry at each location. In this embodiment, a weak base is first added to the lubricating oil circulating within the lubrication system. The weak base reacts with the acids present in the lubricating oil circulating within the system to form a neutral salt of the weak base and the acids. The weak base must contain a sufficient number of carbon atoms to ensure that the neutral salt formed from the acid neutralization is soluble in the oil so that deposits are prevented from forming at the point of acid/base contact. The neutral salt then passes or circulates with the oil to another location within the lubrication system where the salt is contacted with a heterogenous strong base immobilized at this location. The strong base displaces the weak base from the soluble salt and releases the weak base into the oil, leaving behind a salt deposit containing the strong base and the acids. Thus, contact of the neutral salt with the strong base causes a deposit to form where the strong base is located. In this way, deposits resulting from acid neutralization are transferred from one location to another location in the lubrication system of an internal combustion engine.

In yet another embodiment, this invention is a system for reducing piston deposits in an internal combustion engine, said deposits resulting from neutralizing acids present in the lubricating oil of said engine, which comprises

- (a) a lubricating oil that circulates through the lubrication system of the engine,
- (b) a soluble weak base capable of neutralizing acids present in the oil to form soluble neutral salts containing the weak base and the acids, and
- (c) a heterogenous strong base immobilized within the lubrication system of the engine, the strong base being capable of displacing the weak base from the soluble neutral salts such that the weak base is returned to the lubricating oil and the resulting strong base/acid salt is deposited or immobilized with the heterogenous strong base.

When this embodiment is specific to reducing piston deposits, the acid neutralization of step (b) occurs at the piston ring zone of the engine and the heterogenous strong base in step (c) is immobilized outside or downstream of the piston ring zone.

Any of the foregoing embodiments of this invention can be combined with the removal of carcinogenic components from a lubricating oil. For example, polynuclear aromatic hydrocarbons (especially PNA's with at least three aromatic rings) that are usually present in used lubricating oil can be substantially removed (i.e., reduced by from about 60 to about 90% or more) by passing the oil through a sorbent located within the lubrication system through which the oil must circulate after being used to lubricate the engine. The sorbent may be immobilized with the substrate described above or immobilized separate therefrom. Preferably, the substrate and sorbent will be part of the engine filter system for filtering oil. The sorbent can be conveniently located on the engine block or near the sump, preferably downstream of the oil as it circulates through the engine; i.e., after the oil has been heated. Most preferably, the sorbent is downstream of the substrate.

Suitable sorbents include activated carbon, attapulgus clay, silica gel, molecular sieves, dolomite clay, alumina, zeolite, or mixtures thereof. Activated carbon is preferred because (1) it is at least partially selective to the removal of polynuclear aromatics containing more than 3 aromatic rings, (2) the PNA's removed are tightly bound to the carbon and will not be leached-out to become free PNA's after disposal, (3) the PNA's removed will not be redissolved in the used lubricating oil, and (4) heavy metals such as lead and chromium will be removed as well. Although most activated carbons will remove PNA's to some extent, wood and peat based carbons are significantly more effective in removing three and four ring aromatics than coal or coconut based carbons.

The amount of sorbent required will depend upon the PNA concentration in the lubricating oil. Typically, for a five quart oil change, about 20 to 150 grams of activated carbon can reduce the PNA content of the used lubricating oil by up to 90%. Used lubricating oils usually contain from about 10 to about 10,000 wppm of PNA's.

It may be necessary to provide a container to hold the sorbent, such as a circular mass of sorbent supported on wire gauze. Alternatively, an oil filter could comprise the sorbent capable of combining with polynuclear aromatic hydrocarbons held in pockets of filter paper. These features would also be applicable to the substrate.

Any of the foregoing embodiments of this invention can also be combined with a sorbent (such as those described above) that is mixed, coated, or impregnated with additives normally present in engine lubricating oils. In this embodiment, additives (such as the lubricating oil additives described above) are slowly released into the lubricating oil to replenish the additives as they are depleted during operation of the engine. The ease with which the additives are released into the oil depends upon the nature of the additive and the sorbent. Preferably, however, the additives will be totally released within 150 hours of engine operation. In addition, the sorbent may contain from about 50 to about 1.0 wt.% of the additive (based on the weight of activated carbon), which generally corresponds to 0.5 to 1.0 wt.% of the additive in the lubricating oil.

Thus, the various embodiments of this invention can be combined to remove PNA's from a lubricating oil, to extend the useful life of a lubricating oil by releasing conventional additives into the oil, or both.

The present invention may be further understood by reference to the following examples which are not intended to restrict the scope of the claims appended hereto.

Example 1

Six EMA SCOTE engine tests were performed on four different oil formulations using a fuel containing 0.4 wt.% sulfur. An EMA SCOTE test uses a 1Y540 engine that is operated according to the 1-J test procedure developed by the PC-1 committee of A.S.T.M. The essential hardware components of this test include a 1Y704 piston, 1Y702 liner, and 1Y635/1W9460 rings. The engine is operated at 2100 rpm and 70 BHP.

Tests 1 and 2 were run in different engine test stands and at different times than tests 3-6, which were run sequentially in the same test stand. All tests were performed under the same engine test conditions.

Tests 1-3 used a fully formulated 15W/40 premium lubricating oil containing a total of 3.5 wt.% calcium and magnesium phenate detergents. This oil served as a reference oil. For tests 4-6, the phenate detergents were removed from the reference oil and replaced by 0.5 wt.% trioctadecyl amine in the oil, or by zinc oxide pellets (available from Katalco as catalyst 75-1) in the oil filter, or by both. The results obtained from these tests are summarized in Table 1.

TABLE 1

<u>Oil</u>	<u>Reference Oil</u>			<u>Reference Oil w/o Metal Detergents But With</u>		
				<u>Amine + ZnO</u>	<u>Amine</u>	<u>ZnO</u>
Test No.	1	2	3	4	5	6
% TGF (1)	33	26	31	9	42	7
WTD (2)						
1G2 (3)	1308	1286	1051	1239	1660	1293
WD5 (4)	(5)	(5)	414	895	1782	3158

(1) Percent Top Groove Fill is a measure of piston cleanliness.

(2) Weighted Total Demerits is a measure of piston cleanliness.

(3) The % TGF and 1G2 methods of calculating WTD are the current methods of evaluating the SCOTE piston.

(4) The WD5 is a proposed method for calculating WTD that gives greater weight to deposits lower on the piston; e.g., on the upper skirt, pin bases, and undercrown.

(5) Not calculated because the pistons were not rated for the appropriate parts of the piston used in the WD5 rating procedure.

The data in Table 1 show that replacing 3.5 wt. % metal detergent in the oil (Test Nos. 1-3) with 0.5 wt. % ashless amine in the oil plus ZnO pellets in the filter (Test No. 4) markedly improved TGF while maintaining overall piston cleanliness as measured by 1G2. When ZnO pellets were present in the filter with or without tricoctadecyl amine in the oil (Test Nos. 4 and 6), the top of the piston as measured by TGF and the 1G2 method of calculating WTD was relatively clean. However, when the amine was not present (Test No. 6), the bottom of the piston (especially the upper skirt, pin bore and undercrown which are part of the WD5 method of calculating WTD) was very dirty. When ZnO is not present (Test No. 5), the top of the piston is dirty as shown by the 42% TGF. Thus, both the weak base (the amine) and the strong base (the ZnO) are necessary for control of piston cleanliness.

In addition to keeping the piston clean, a lubricant must control the loss in oil basicity (i.e., TBN), the gain in acidity (i.e., TAN), engine wear as measured by ppm Fe in the oil, and the formation of insoluble species in

the oil as measured by pentane insolubles. The changes in these factors for certain of the oils tested are shown in Figures 1-4.

Figure 1 illustrates that the lubricating oil containing the amine with ZnO in the filter (Test No. 4) had less loss of TBN (as measured by ASTM 2896) than the reference oil containing the metal detergents (Test No. 3).

Figure 2 illustrates that the rate of increase in TAN (as measured by ASTM D664) is less for Test No. 4 oil than for the Test No. 3 oil (with metal detergent), less than for Test No. 5 oil (with only amine in the oil and no ZnO in the filter), and less than for Test No. 6 oil (with no amine or metal detergents in the oil but with ZnO in the filter). This demonstrates control of engine acid corrosion by the present weak base/strong base system.

Figure 3 illustrates that operating the SCOTE engine on Test No. 4 oil produced at least as little soluble Fe (measured by atomic emission spectroscopy) as did the Test No. 3 oil and less than the Test No. 5 oil (with only amine in the oil and no ZnO in the filter) and Test No. 6 oil (with no amine or ash detergent in the oil but with ZnO in the filter). This demonstrates control of engine acid corrosion by the present weak base/strong base system.

Figure 4 illustrates that insolubles (measured by ASTM D893B as pentane insolubles) in the oil were controlled as well by replacing ash detergent with trialkyl amine in conjunction with ZnO in the filter (Test No. 4) as by the ash detergent (test oil 3). Control of insolubles was poorer when either the amine was used without ZnO (Test No. 5) or ZnO was used without the amine (Test No. 6).

Example 2

Piston deposits from Tests 3 and 4 of Example 1 were analyzed for sulfur by x-ray. The results obtained are shown in Table 2.

Table 2

Test No.	3	4	Sulfur Reduction, %
Piston sulfur, wt. %			
Top Groove	0.79	0.27	66
2nd Hand	2.89	1.41	50
2nd Groove	0.62	0.35	44

The data in Table 2 show that there is significantly less sulfur on the piston from Test No. 4 (amine + ZnO) than on a piston from Test No. 3 (reference oil).

In addition, no deposits were collected in the engine filter during Test No. 3. However, in Test No. 4, 183.2 g of ZnO pellets were placed in the filter. At the end of Test No. 4, the pellets were removed from the filter and repeatedly washed with heptane to remove oil. After six heptane washes and air drying, the pellets were reweighed and found to have increased in weight by 21%. In addition to the measured weight gain, there were losses of pellets during removal of the pellets from the filter at the completion of the test. Heating a portion of the used pellets to 900°C to remove organic material resulted in a 30% reduction in weight. Therefore, a significant amount of material (21-30%) was deposited on the pellets during the engine test. A photo acoustic IR (infrared) of the used pellets found strong absorbances at 1200 cm⁻¹, which is typical of alkyl sulphates and sulfonates. This confirms that deposits were transferred from the piston to the filter.

Claims

1. A method for reducing piston deposits in an internal combustion engine lubricated with a lubricating oil containing a soluble weak base and circulating within the lubrication system of the engine which comprises

(a) circulating the lubricating oil to the piston ring zone of the engine where fuel combustion acids are introduced into the oil,

(b) contacting, at the piston ring zone, the combustion acids with the weak base such that at least a portion of the acids are neutralized to form a soluble neutral salt containing the weak base and the combustion acids,

the oil as measured by pentane insolubles. The changes in these factors for certain of the oils tested are shown in Figures 1-4.

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Claims

1. A method for reducing piston deposits in an internal combustion engine lubricated with a lubricating oil containing a soluble weak base and circulating within the lubrication system of the engine which comprises
 - (a) circulating the lubricating oil to the piston ring zone of the engine where fuel combustion acids are introduced into the oil,
 - (b) contacting, at the piston ring zone, the combustion acids with the weak base such that at least a portion of the acids are neutralized to form a soluble neutral salt containing the weak base and the combustion acids,



(c) circulating the lubricating oil containing the soluble neutral salt to a heterogeneous strong base immobilized within the lubrication system of the engine downstream of the piston ring zone, and

(d) contacting the soluble neutral salt with the heterogeneous strong base, thereby causing at least a portion of the weak base in the salt to be displaced into the lubricating oil and resulting in the formation of a strong base/combustion acid salt which is immobilized with the heterogeneous strong base.

2. The method of claim 1 wherein the weak base is or comprises a dialkyl amine, a trialkyl amine e.g., trihexyl amine, trioctadecyl amine, or mixtures thereof, a dialkyl phosphine, a trialkyl phosphine, or mixtures thereof.

3. The method of claim 1 or claim 2 wherein the strong base is or comprises barium oxide, calcium carbonate, calcium hydroxide, calcium oxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium aluminate, sodium carbonate, sodium hydroxide, zinc oxide, or mixtures thereof.

4. The method of any one of claims 1 to 3 wherein the heterogeneous strong base is incorporated on a substrate.

5. The method of claim 4 wherein the substrate is alumina, activated clay, cellulose, cement binder, silica-alumina, activated carbon, or mixtures thereof.

6. The method of claim 5 wherein the substrate is part of the oil filter system of the engine.

7. The method of any one of claims 1 to 6 wherein polynuclear aromatic compounds are also removed from the lubricating oil by contacting the oil with a sorbent located within the lubrication system.

8. The method of claim 7 wherein the sorbent and heterogeneous strong base are included within the oil filter system of the engine.

9. The method of claim 7 or claim 8 wherein the sorbent is impregnated with at least one engine lubricating oil additive.

10. A system for reducing deposits in an internal combustion engine, said deposits resulting from neutralizing acids present in the lubricating oil of said engine, which comprises :

(a) a lubricating oil that circulates through the lubrication system of the engine;

(b) a soluble weak base capable of neutralizing acids present in the oil to form soluble neutral salts containing the weak base and the combustion acids; and

(c) a heterogeneous strong base immobilized within the lubrication system of the engine, the strong base being capable of displacing the weak base from the soluble neutral salts such that the weak base is returned to the lubricating oil and the resulting strong base/acid salt is immobilized with the heterogeneous strong base.

11. The system of claim 10 wherein the weak base and strong base are defined as any one of claims 1 to 9.

12. A method for transferring deposits from one location in the lubrication system of an internal combustion engine to another location within the lubrication system, the deposits resulting from neutralizing acids present in the lubricating oil circulating within the lubrication system, which comprises :

(a) adding a soluble weak base to the lubricating oil;

(b) contacting the weak base with the acids at a first location within the lubrication system, thereby neutralizing the acids and forming a soluble neutral salt containing a weak base and the acids; and

(c) contacting the soluble neutral salt with a heterogeneous strong base immobilized at a second location within the lubrication system, thereby displacing at least a portion of the weak base from the neutral salt into the oil and forming a strong base/acid salt which is immobilized with the heterogeneous strong base.

13. The method of claim 12 wherein the weak base and the strong base are defined as any one of claims 1-9.

Patentansprüche

1. Verfahren zur Verringerung von Kolbenrückständen in einem Verbrennungsmotor, der mit einem Schmieröl geschmiert ist, das eine lösliche, schwache Base enthält und innerhalb des Schmiersystems des Motors zirkuliert, bei dem

(a) das Schmieröl zu der Kolbenringzone des Motors zirkuliert wird, wo in das Öl Kraftstoffverbrennungssäuren eingeführt werden,

(b) die Verbrennungssäuren an der Kolbenringzone mit der schwachen Base kontaktiert werden, so daß mindestens ein Teil der Säuren neutralisiert wird, um ein lösliches, neutrales Salz zu bilden, das die schwache Base und die Verbrennungssäuren enthält,

(c) das das lösliche, neutrale Salz enthaltende Schmieröl zu einer heterogenen, starken Base zirkuliert wird, die innerhalb des Schmiersystems des Motors stromabwärts von der Kolbenringzone immobilisiert



ist, und

(d) das lösliche, neutrale Salz mit der heterogenen, starken Base kontaktiert wird, was die Verdrängung mindestens eines Teils der in dem Salz enthaltenen, schwachen Base in das Schmieröl bewirkt und zur Bildung eines Salzes aus starker Base/Verbrennungssäure führt, das mit der heterogenen, starken Base immobilisiert wird.

2. Verfahren nach Anspruch 1, bei dem die schwache Base ein Dialkylamin, ein Trialkylamin, z.B. Trihexylamin, Trioctadecylamin oder eine Mischung derselben, ein Dialkylphosphin, ein Trialkylphosphin oder eine Mischung derselben ist oder umfaßt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem die starke Base Bariumoxid, Calciumcarbonat, Calciumhydroxid, Calciumoxid, Magnesiumcarbonat, Magnesiumhydroxid, Magnesiumoxid, Natriumaluminat, Natriumcarbonat, Natriumhydroxid, Zinkoxid oder eine Mischung derselben ist oder umfaßt.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die heterogene, starke Base auf einem Substrat eingeführt wird.

5. Verfahren nach Anspruch 4, bei dem das Substrat Aluminiumoxid, aktivierter Ton, Cellulose, Zementbinder, Siliciumdioxid-Aluminiumoxid, aktivierter Kohlenstoff oder eine Mischung derselben ist.

6. Verfahren nach Anspruch 5, bei dem das Substrat Teil des Ölfiltersystems des Motors ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem aus dem Schmieröl auch mehrkernige aromatische Verbindungen entfernt werden, indem das Öl mit einem innerhalb des Schmiersystems angeordneten Sorbens kontaktiert wird.

8. Verfahren nach Anspruch 7, bei dem das Sorbens und die heterogene, starke Base in dem Ölfiltersystem des Motors eingeschlossen sind.

9. Verfahren nach Anspruch 7 oder Anspruch 8, bei dem das Sorbens mit mindestens einem motorschmieröladditiv imprägniert ist.

10. System zur Verringerung von Ablagerungen in einem Verbrennungsmotor, wobei die Ablagerungen von der Neutralisation von in dem Schmieröl des Motors vorhandenen Säuren herrühren, das:

(a) ein Schmieröl, das durch das Schmiersystem des Motors zirkuliert,

(b) eine lösliche, schwache Base, die in der Lage ist, in dem Öl vorhandene Säuren zu neutralisieren, um lösliche, neutrale Salze zu bilden, die die schwache Base und die Verbrennungssäuren enthalten, und

(c) eine heterogene, starke Base umfaßt, die innerhalb des Schmiersystems des Motors immobilisiert und in der Lage ist, die schwache Base aus den löslichen, neutralen Salzen zu verdrängen, so daß die schwache Base in das Schmieröl zurückgeführt wird und das resultierende Salz aus starker Base/Säure mit der heterogenen, starken Base immobilisiert wird.

11. System nach Anspruch 10, bei dem die schwache Base und die starke Base wie in einem der Ansprüche 1 bis 9 definiert sind.

12. Verfahren zur Überführung von Ablagerungen von einer Stelle in dem Schmiersystem eines Verbrennungsmotors zu einer anderen Stelle innerhalb des Schmiersystems, wobei die Ablagerungen von der Neutralisation von Säuren herrühren, die in dem Schmieröl vorhanden sind, das in dem Schmiersystem zirkuliert, bei dem:

(a) dem Schmieröl eine lösliche, schwache Base zugesetzt wird,

(b) die schwache Base mit den Säuren an einer ersten Stelle innerhalb des Schmiersystems kontaktiert wird, wodurch die Säuren neutralisiert werden und ein lösliches, neutrales Salz gebildet wird, das eine schwache Base und die Säuren enthält, und

(c) das lösliche, neutrale Salz mit einer heterogenen, starken Base kontaktiert, die an einer zweiten Stelle innerhalb des Schmiersystems immobilisiert ist, wodurch mindestens ein Teil der schwachen Base aus dem neutralen Salz in das Öl verdrängt und ein Salz aus starker Base/Säure gebildet wird, das mit der heterogenen, starken Base immobilisiert wird.

13. Verfahren nach Anspruch 12, bei dem die schwache Base und die starke Base wie in einem der Ansprüche 1 bis 9 definiert sind.

Revendications

1. Un procédé pour la réduction des dépôts sur les pistons dans les moteurs à combustion interne lubrifiés par une huile de graissage contenant une base faible soluble et circulant dans le circuit de graissage du moteur, comprenant

(a) la circulation de l'huile de graissage vers la zone des segments des pistons du moteur où les acides de combustion du carburant sont introduits dans l'huile,

(b) la mise en contact, dans la zone des segments des pistons, des acides de combustion avec la base



faible, de manière qu'au moins une partie des acides soit neutralisée sous forme d'un sel neutre soluble contenant la base faible et les acides de combustion,

(c) la circulation de l'huile de graissage contenant le sel neutre soluble sur une base acide forte hétérogène, immobilisée dans le circuit de graissage du moteur, en aval de la zone des segments des pistons, et

(d) la mise en contact du sel neutre soluble avec la base forte hétérogène, de manière à provoquer le déplacement d'au moins une partie de la base faible du sel dans l'huile de graissage et à provoquer la formation d'un mélange sel de combustion acide/base forte, immobilisé dans la base forte hétérogène.

2. Le procédé selon la revendication 1, dans lequel la base faible est ou comprend une dialkylamine, une trialkylamine, telle qu'une trihexylamine, une trioctadecylamine ou leurs mélanges, une dialkylphosphine, une trialkylphosphine ou leurs mélanges.

3. Le procédé selon la revendication 1 ou 2, dans lequel la base forte est ou comprend de l'oxyde de baryum, du carbonate de calcium, de l'hydroxyde de calcium, de l'oxyde de calcium, du carbonate de magnésium, de l'hydroxyde de magnésium, de l'oxyde de magnésium, de l'aluminate de sodium, du carbonate de sodium, de l'hydroxyde de sodium, de l'oxyde de zinc ou leurs mélanges.

4. Le procédé selon l'une quelconque des revendications 1 à 3, dans lequel la base forte hétérogène est incorporée dans un substrat ou support.

5. Le procédé selon la revendication 4, dans lequel le substrat est de l'alumine, de l'argile activée, de la cellulose, un liant de ciment, de silica-alumine, du carbone activé ou leurs mélanges.

6. Le procédé selon la revendication 5, dans lequel le substrat fait partie du circuit de filtre à huile du moteur.

7. Le procédé selon l'une quelconque des revendications 1 à 6, dans lequel les composés aromatiques polynucléaires sont également enlevés de l'huile de graissage par la mise en contact de l'huile avec un sorbant placé dans le circuit de graissage.

8. Le procédé selon la revendication 7, dans lequel le sorbant et la base forte hétérogène sont compris dans le circuit de filtre à huile du moteur.

9. Le procédé selon la revendication 7 ou 8, dans lequel le sorbant est imprégné d'au moins un additif pour huile de graissage du moteur.

10. Un système de réduction des dépôts dans un moteur à combustion interne, lesdits dépôts résultant de la neutralisation des acides présents dans l'huile de graissage du moteur, comprenant:

(a) une huile de graissage circulant dans le circuit de graissage du moteur;

(b) une base faible soluble, capable de neutraliser les acides présents dans l'huile pour former des sels neutres solubles contenant la base faible et les acides de combustion; et

(c) une base forte hétérogène immobilisée dans le circuit de graissage du moteur, la base forte étant capable de déplacer la base faible des sels solubles neutres, de manière à renvoyer la base faible dans l'huile de graissage et que le mélange sel acide/base forte résultant soit immobilisé dans la base forte hétérogène.

11. Le système selon la revendication 10, dans lequel la base faible et la base forte sont définies par l'une quelconque des revendications 1 à 9.

12. Un procédé de transfert des dépôts d'un emplacement du circuit de graissage d'un moteur à combustion interne vers un autre emplacement du circuit de graissage, les dépôts résultant de la neutralisation des acides présents dans l'huile de graissage circulant dans le circuit de graissage, comprenant:

(a) l'addition d'une base faible soluble à l'huile de graissage;

(b) la mise en contact de la base faible avec les acides dans un premier emplacement du circuit de graissage, de manière à neutraliser les acides et à former un sel neutre soluble comprenant la base faible et les acides; et

(c) la mise en contact du sel neutre soluble avec la base forte hétérogène immobilisée dans un second emplacement à l'intérieur du circuit de graissage, de manière à déplacer au moins une partie de la base faible du sel neutre dans l'huile et à former un mélange base forte/sel acide, immobilisé dans la base forte hétérogène.

13. Le procédé selon la revendication 12, dans lequel la base faible et la base forte sont définis par l'une quelconque des revendications 1 à 9.

