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NEUTRALIZATION OF LUBRICATING OILS

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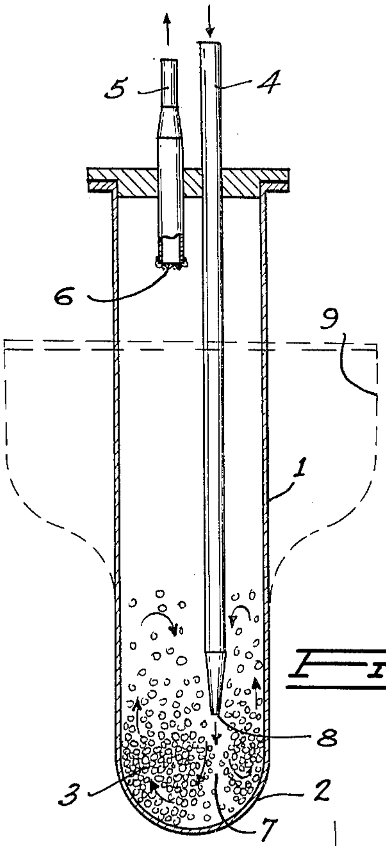

Fig. 1.

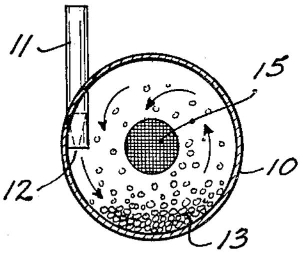

Fig. 3.

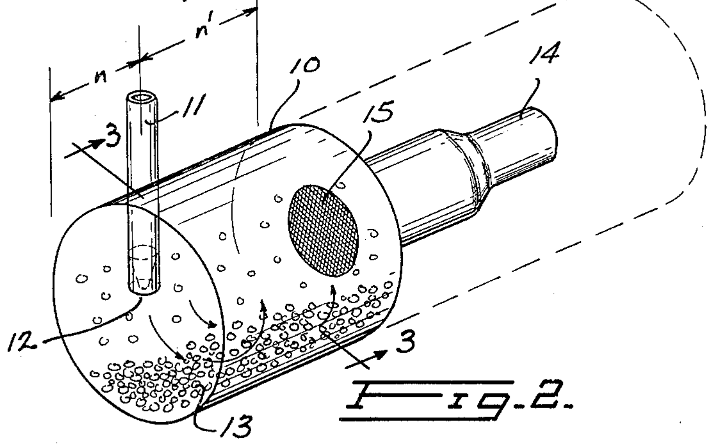

Fig. 2.

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NEUTRALIZATION OF LUBRICATING OILS

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This invention relates to the treatment of mineral or lubricating-type oils to counteract deterioration thereof and prevent the build-up of acid or acid-acting compounds therein. In particular the invention provides a process, a particulate treating agent, and an apparatus for the continual treatment of the oils with alkaline-acting metals selected from the group consisting of Li, Na, Ca, Sr, Ba and their alloys—providing a "trickle charge" alkalinity.

Lubricating oils are frequently compounded with alkaline "buffers" to prevent acidity. However, these additives become depleted in use, and while the oil may otherwise be satisfactory, acid build-up makes discard or reclamation necessary. It has been previously proposed to contact lubricating oil during use with certain alkaline-acting metals or alloys thereof. The equivalent of sacrificial corrosion is believed to take place, with acids (or other corrosive substances such as sulfur ocmpounds) combining with the metal. For continual effectiveness the corrosion product formed must dissolve or disperse in the oil. This ability to dissolve or disperse is dependent on many factors, but particularly temperature. It has been found that under operating conditions where the temperature is varied considerably and where frequent operation at low temperatures is carried out (particularly intermittent operation), the corrosion products are in sufficiently soluble or dispersible. It has further been found that even at elevated operating temperatures and even when the surface area of the metals or alloys is relatively high, the effectiveness thereof becomes impaired before being used up and before replacement is necessary. This impairment is due to the formation of a gummy adherent coating on the metal surface which eventually completely isolates the metal surface from the oil, and resists even the action of rapidly flowing oil.

An object of this invention is to provide an oil treatment process with alkaline-acting metals in which the formation or accumulation of an adherent inert coating is prevented. A further object is to provide a process in which particles of certain alkali or alkaline earth metals or alloys containing these metals are caused to tumble rapidly and abrade each other continually. A further object is to provide an apparatus in which controlled oil flow is used to agitate and tumble the particles and cause self-abrasion thereof, the apparatus being specially adapted for intermittent and low temperature use. A further object is to provide a particulate treating agent comprising certain alkali or alkaline earth metals or alloys thereof dispersed in a solid non-metallic abradable matrix material which may either be inert or be itself a desirable additive or treating agent.

It has now been found that the effectiveness of the particulate treating agent can be prolonged until the agent is exhausted by causing the particles to be agitated in a manner to cause controlled tumbling and self-abrasion thereof. This movement of the particles may be effected by mechanical agitation. However, it is more desirable to use the kinetic energy of the oil circulating in the system to cause a self-abrading tumbling movement.

The apparatus is illustrated in FIGURES 1, 2, and 3 wherein:

FIG. 1 is a vertical secton of one reactor chamber in which the oil is injected vertically downward and into a bed of the particulate metal agent.

FIG. 2 is a perspective exposed view of another reactor chamber in which the oil is injected tangentially to the chamber walls.

FIG. 3 is a vertical section on line 3—3 of FIG. 2

Referring to FIG. 1 this embodiment comprises a cylindrical chamber **1**, with a hemispherical-shaped bottom **2**. The metal treating agent is in the form of "shot" **3** in bottom portion **2**. The oil is introduced as a jet **7** downwardly into the central region of the bed of "shot" by means of inlet tube **4** having orifice **8**. The treated oil is led from the chamber through exit tube **5**. A screen **6**, to retain any particulate material is shown at the intake of tube **5**. In operation the oil jet **7** causes the "shot" **3** to tumble and abrade each other in the manner shown by the arrows. Optionally a flared top portion **9** may be used to minimize entraining particles in the exit flow.

Referring to FIGS. 2 and 3, a horizontal-disposed cylindrical chamber **10** is fitted with an inlet tube **11** entering tangentially into the cylinder. The orifice **12** of the inlet tube **11** should desirably be directed downwardly where intermittent operation is intended. The particulate treating agent **13** is agitated by the oil jet in the manner shown by the arrows to cause effective self-abrasion. The treated oil is removed through screen **15** and exit tube **14**, which is desirably of relatively large cross-section to minimize collection of the particles near the exit. The distance "*n*" can be less or greater than "*n'*," particularly if the orifice enters tangentially near the 12 o'clock position. It is preferred that the orifice enter near the 9 o'clock position as shown, and that "*n*" be approximately equal to "*n'*." This embodiment can be modified by disposing the cylinder vertically and introducing the oil jet tangentially near the bottom thereof. It has been found that inlet orifices directed upwardly tend to clog or plug during shut-down periods. It may be desirable to use a plurality of jets and/or exit tubes suitably positioned in the chamber. The treating chambers may be incorporated in the oil filter circuit of an internal combustion engine—desirably on the input side of the filter. The chamber can be combined with the oil filter e.g. as a sump chamber or a top chamber. Dotted line **16** in FIG. 2 indicates an optional combined oil filter.

Generally it has been found satisfactory to use jet inlet orifices of about 1/16" to about 1/4" diameter. Oil flow rate through these orifices may desirably be within the range of about 0.3 to about 2 gal./min. or higher. The particle size of the metal treating agent is chosen to give the desired active surface area and rate of abrasion (life) without becoming entrained or suspended in the oil. The rate of abrasion depends on the acidity and flow rate of the oil, and on the brittleness and size of the particles, and is desirably adjusted by changing the inlet orifice size or particle size or both to give the required elevation of pH in the oil. A particle size of -3 $+20$ mesh (Tyler) is preferred although particles up to 0.5" cubes have been used successfully. Particles below the 0.03" average diameter tend to become entrained in the oil. The particles can be of any suitable shape. The specific gravity of the particle should preferably differ by at least 10% from that of the oil. If the particles are lighter than the oil, an apparatus such as in FIG. 1, but inverted, may be used. Apparatus as shown in FIG. 2 is satisfactory with all densities of treating material.

If it is desirable to increase the rate of abrasion, abrading members can be attached to the inside of the chamber, or the interior surface of the chamber roughened. The interior surface may also be coated with a layer containing particles of the alkaline-acting metal.

The attrition caused by the frictional contact between the tumbling particles maintains fresh and active surfaces of the metal treating agent. The abrasive action at the site of formation of the corrosion products also assists in the dissolution or dispersion of these products, particularly at low temperatures. Compared to mechanical agitation, the degree and uniformity of the abrasion is more desirable when caused and controlled by the oil flow.

The alkaline-acting particulate treating agents comprise at least one of the metals Li, Na, Ca, Sr, Ba, and alloys thereof. The particles are selected from the group consisting of:

(a) Metals Li, Na, Ca, Sr, and Ba,
(b) Alloys of at least one of the alkali metals Li and Na with at least one of the group zinc, aluminum, tin, lead, antimony, bismuth, magnesium, and the alkaline earth metals, and
(c) Any of the above metals (a) or alloys (b) dispersed in a solid non-metallic abradable matrix material which is harmless to moving metal parts.

The term "alloy" is intended to include mixtures or dispersions. The alloys (b) and composite particles (c) should contain at least about 15 vol. percent of metal (a) above. Examples of alloys are as follows: Li–Mg alloys, Li–Na–Mg alloys, Li–Zn alloys, Li–Al alloys, Na–Pb alloys, Na–Bi and Na–Sn–Pb alloys.

Suitable matrix materials include hard waxes, thermoplastic and thermosetting resins, and solid surface-active agents. These matrix materials should have a melting point above 100° C. and not inactivate the dispersed metal. The matrix should abrade or "corrode" at approximately the same rate as the metal. Examples of matrix materials are polyolefins, damar wax, wax-polyolefin blends, epoxy and melamine-aldehyde resins and hard soaps. The soaps may be Li or Ba soaps of higher fatty acids, rosin acids, naphthenic acids, and dimeric acids. The polyolefin may be for instance a polyethylene, polypropylene, polystyrene or polyalphamethylstyrene. The dispersion of active metal in the matrix may be made by any suitable method. The matrix serves to encapsulate the metals which are reactive with moisture, and simplifies handling of the particles before use.

The composite treating agents should contain at least about 15 vol. percent (based on total particle volume) usually 20–80 vol. percent depending on the activity de-

sired, of alkali or alkaline earth metal selected from the group Li, Na, Ca, Sr, and Ba. The amount of treating agent is selected to maintain the required elevation of pH for the necessary period of operation. This amount will depend on the metal equivalent weight and the corrosion rate. An approximate range can be indicated as about 10 to about 80 gms. (based on calcium) of metal (a) above, per gallon of oil treated, appropriate adjustment according to equivalent weight being made for the metals Li, Na, Sr, and Ba. Less of the active metal can be used in conjunction with the tumbling self-abrading action of the present invention than is necessary in prior art processes where there is no such action. The use of alloying elements such as zinc and magnesium which also have neutralizing capacity is desirable, rather than inert diluents such as lead. Some metals or alloys such as Ca are useful in a tumbling abrading environment which otherwise would passivate almost immediately by an inert coating. Treating agents such as metallic Na and its alloys also remove corrosive sulfur from oils and reduce high sulfur corrosion values to acceptable limits. The preferred metals or alloys are Li, Ca, Ba, Li–Mg alloys, Li–Zn alloys and Li–Al alloys. The preferred matrix is paraffin wax-polyethylene blend wherein the polyethylene is present in minor amounts and acts to harden the blend. The higher melting waxes and the high density, high melting polyethylenes are preferred.

The following examples illustrate the invention. Acidity of the oils treated was assessed as the number on the pH scale of a laboratory pH meter when 2 grams of the oil were dissolved in 10 grams of benzene-isopropyl alcohol (50:50) containing 1% water. Used crankcase oil gave readings in the range 4.0–6.5 depending on source. Unused oils usually gave readings in the range 7–9 depending on their formulation. The oil treated in these examples was a used automotive crankcase oil.

EXAMPLE 1

A metal cylinder 2.5 in. in diameter, 3.0 in. in length, disposed horizontally as in FIG. 2, and having an inlet orifice 0.12 in. in diameter directed tangentially downward at the 2 o'clock position, was used for these tests. A laboratory centrifugal pump provided oil circulation from a 0.5 gallon reservoir of oil which was maintained at about 80° C. The oil temperature was maintained at 80° C., throughout the system. The cylinder and the remainder of the system contained about 0.5 gal. oil. Air was bubbled continuously through the oil in the reservoir to promote continuous development of acidity. Where no treating agents were used the pH decreased to about 4.5 and detrimental sludge formation occurred. Results are summarized in Table I.

Table I

OIL TREATMENT WITH ALKALINE-ACTING METALS

Time, hr.	Oil Flow, gal./min.	Metal or Alloy, Vol. Percent	Wt. Total Particles, gm.	Initial pH	pH after treatment	Remarks
5	0.7	23% Sodium	26	6.2	8.1	26% particle weight consumed.
20	0.7	77% Lead			8.7	
18	0.6	68% Lithium	12	6.2	7.2	
42	0.6	32% Zinc			8.0	
18	0.6	50% Lithium	12	6.2	7.2	
42	0.6	50% Zinc			8.0	
72	0.6	63% Lithium	14	4.7	4.8	No abrasion particles unconsumed. 5.7% particle weight consumed.
20	1.2	37% Magnesium		5.9	8.4	
24	1.2	77% Lithium 23% Aluminum	10	3.7	8.3	5% particle weight consumed.
3	1.7	Lithium	10	5.3	9.0	8% particle weight consumed.
16	1.6	Barium	15	5.9	7.4	
16	1.6	Strontium	18.5	5.9	7.7	10% particle weight consumed.
2	0.5	Calcium	21.4	5.1	7.5	0.02% water in oil.

EXAMPLE 2

Suspensions of Li or Na in various matrices were prepared by gently dispersing the molten metal in a molten matrix material. In preparing such suspensions the metal need not be melted. A styrene monomer was mixed with metal and polymerized in situ in other instances (Li or Na metal catalyzing the reaction). The same oil treating apparatus as in Example 1 was used. Some typical results are shown in Table II.

Table II

OIL TREATMENT WITH ALKALINE-ACTING METALS IN MATRICES

Time, hr.	Oil Temp., ° C.	Oil Flow, gal./min.	Metal and Matrix, Vol. percent[1]	Wt. Total Particles gm.	Initial pH	pH after treatment
1	75	0.8	59% Lithium 35% Paraffin Wax 6% Polyethylene	10	5.5	6.1
2	75	0.8	59% Lithium 35% Paraffin Wax 6% Polyethylene	10	5.5	7.4
4	75	0.8	59% Lithium 35% Paraffin Wax 6% Polyethylene	10	5.5	8.9
4	78	0.9	18% Lithium 82% Polymethyl Styrene	20	5.3	8.1
10	82	1.3	25% Sodium 75% Epoxy Resin	18	5.2	7.4
5	82	0.9	25% Lithium 75% Lithium Stearate	15	4.2	7.8
9	80	1.1	28% Lithium 72% Polystyrene	16	5.3	8.0

[1] Subdivided metal suspended in solid matrix.

The results in Tables I and II show that treatment according to the invention resulted in significant increases in the pH. For tough light metals such as Li–Mg alloys, higher flow rates are usually necessary to give the necessary abrasion—compared to less tough, heavier metals. For Ca metal the addition of 0.01–2% of water (as normally occurs in most oil in use) increased the rate of corrosion and raised the pH above 7. Two hours operation usually gave a substantial proportion (about 50%) of the final alkalinity increase. The same particles could be used to treat consecutive samples of the "used" oil with the same results indicating that the tumbling, self-abrading bed was successfully keeping the particle surfaces active. The reactors showed no tendency to clog or otherwise become less effective after shut-down. The following metals per se showed a small effect only and would not be advantageous: Mg, Zn, and Al. Na is not as desirable as Li or Ba in some applications since the Na corrosion products are water-soluble and tend to form emulsions. For most practical applications, it is desirable that the particulate treating agents should be able to maintain the oil at a pH of about 7 or above.

EXAMPLE 3

Table III lists comparative tests with some of the metals and alloys *not* allowed to tumble and abrade. Except where indicated, the procedure and apparatus employed was the same as in Example 1. The rate of flow the oil through the particles was comparable to the rates in Tables I and II, but an inlet orifice to the reactor of 0.375 in. diameter was used to reduce the oil velocity. The particles in the bed remained virtually stationary during the tests. The pH showed little or no increase on treatment and in some instances actually decreased when the particles did not tumble and self-abrade.

Mixtures of different treating agents may be used for various desired effects. For instance the bed may comprise a minor amount of particles which abrade rapidly and cause an initial rapid rise in pH (e.g. lithium shot), together with particles which abrade slowly and maintain the elevated pH (e.g. lithium-aluminum alloy shot). Where metals of different electropositivity are used simultaneously there is usually a slightly more rapid overall corrosion rate.

Table III

OIL TREATMENT WITH ALKALINE-ACTING METALS NOT ALLOWED TO TUMBLE AND ABRADE

Time, hr.	Oil Temp., ° C.	Oil Flow, gal./min.	Metal or Alloy, Vol. percent	Total Wt. Particles, gms.	Initial pH	pH after treatment
24	80	1.0	Strontium	15	6.7	6.6
26	80	1.0	Barium	12	5.4	5.2
96	80	1.0	Lithium	5	6.1	5.5
34	80	1.0	77% Lithium 23% Aluminum	9	5.3	5.3
40	82	1.0	63% Lithium 37% Magnesium	10	4.8	5.0
48	80	1.0	50% Lithium 50% Zinc	10	4.7	4.6
24	80	1.2	59% Lithium[1] 35% Paraffin Wax 6% Polyethylene	12	6.1	6.2

[1] Sub-divided lithium suspended in wax-polyethylene blend.

Barium and zinc compounds are commonly added to lubricating oils as dispersants and anti-friction agents respectively. The barium and zinc becomes depleted in normal use mainly due to inclusion in sludge. A mixed tumbling and abrading bed can be used to prevent depletion of one or both of barium and zinc and to maintain an elevated pH. The following example illustrates this mixed bed treatment.

EXAMPLE 4

Pure mineral oil containing no additives, having a pH of 7.1, a viscosity of 200 S.U.S. at 100° F., and a viscosity index of 70 was passed through an apparatus similar to that shown in FIGURE 2. The oil temperature was maintained at 80° C. and air was passed at a constant slow rate into the oil as it contacted the bed. A blank experiment was conducted in which no metal bed was used—the pH falling continually from 7.1 to 5 in 90 hours. When a mixed tumbling and abrading bed of particles of barium and zinc in equal weights was used, the pH of the oil was found to increase from 7.1 to 8.6

in 2 hours. At this time the oil contacting the bed was allowed to settle, and two samples were withdrawn. One sample was centrifuged to optical clarity, the supernatant liquid being decanted and ashed. The second sample was ashed directly. The centrifuged sample contained 0.1% ash compared to 0.3% ash for the second sample. In both cases the ratio of barium to zinc in the ash was 9 to 1. Thus the treatment not only elevated the pH, but also introduced significant quantities of the desirable metals into solution in the oil.

The invention is applicable to transformer, fuel, and heat transfer oils as well as lubricating-type oils. It is also useful in sweetening crude oils.

We claim:

1. A method of treating oil which comprises circulating the oil through a zone in which particles are in tumbling and self-abrading motion, said particles containing one of the group consisting of (a) the metals Li, Na, Ca, Sr, Ba, and (b) alloys of at least one of the alkali metals Li and Na with at least one of the group consisting of zinc, aluminum, tin, lead, antimony, bismuth, magnesium and the alkaline earth metals; said metal (a) being present in at least 15 vol. percent.

2. A method of counteracting deterioration of oil by treatment with alkaline-acting metals which comprises continually feeding the oil through a jet orifice into a bed of particles containing one of the group consisting of (a) the metals Li, Na, Ca, Sr, Ba, and (b) alloys of at least one of the alkali metals Li and Na with at least one of the group consisting of zinc, aluminum, tin, lead, antimony, bismuth, magnesium and the alkaline earth metals; said metal (a) being present in at least 15 vol. percent, at a velocity sufficient to cause the particles to undergo tumbling and self-abrading motion.

3. The method of claim **2** wherein the bed comprises a mixture of particles which abrade rapidly and cause an initial rapid rise in pH, and particles which abrade slowly.

4. The method of claim **2** wherein the particles contain said alkaline-acting metal dispersed in a solid non-metallic abradable matrix harmless to moving metal parts.

5. The method of claim **2** wherein said bed contains mixed particles of different metals.

6. A particulate treating agent for counteracting deterioration of oils comprising a solid matrix material melting above about 100° C. and consisting essentially of a wax-polyolefin blend, having dispersed therein discrete particles selected from the group consisting of (a) the metals Li, Na, Ca, Sr, Ba, and (b) alloys of at least one of Li and Na with at least one of the group consisting of zinc, aluminum, tin, lead, antimony, bismuth, magnesium and the alkaline earth metals said metal (a) being present in from 20 to 80 vol. percent.

7. A particulate treating agent for counteracting deterioration of oils comprising a solid matrix material melting above about 100° C. consisting essentially of a blend of wax and a minor amount of polyethylene, having dispersed therein discrete particles comprising Li, the Li being present in from 20 to 80 vol. percent.

8. A reactor for contacting oil with particles containing an alkaline-acting metal comprising (a) an enclosed chamber having a wall portion rounded in at least one dimension, (b) a bed of said particles in the rounded portion of said chamber, (c) the rounded portion of the chamber containing said bed being coated with an adherent abrasive layer, (d) an inlet tube having a jet orifice adapted to direct a stream of the oil to be treated into the central region of said bed, said jet orifice entering tangentially where the wall portion containing said bed is rounded in one dimension only, the oil velocity being sufficient to cause a tumbling and self-abrading motion of the particles in said bed, and (e) an exit tube for the treated oil, of relatively large cross-section compared to the jet orifice, located remote from said bed.

9. A particulate treating agent for counteracting deterioration of oils comprising a solid matrix material melting above about 100° C. consisting essentially of a blend of wax and a minor amount of polyethylene, having dispersed therein discrete particles comprising Na, the Na being present in from 20 to 80 vol. percent.

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