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REMOVAL OF ACIDIC SUBSTANCES FROM USED LUBRICATING OIL EMPLOYING FATTY ACID SALTS OF BARIUM, CALCIUM AND STRONTIUM

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This invention has to do with the lubrication of heavy duty engines of the diesel type, typified by, but not limited to marine diesel engines.

In such engines the fuel is a heavy hydrocarbon product, often a residual oil, and frequently an oil of high sulphur content, known in the industry as a "sour" oil. Price considerations operate against the provision of bunker oils from which sulphur has been removed, and even if such oils could be purchased in some areas, questions of geography and local supply would cause the use of sour bunker oils to a great extent.

The burning of such fuels in the combustion chambers of the engines gives rise to acidic constituents in the combustion gases and unavoidable "blow-by" introduces these gases into the crankcase, where the acidic materials build up in the crankcase oil. If not removed, serious corrosion results in bearings, shafts, and other parts lubricated by the crankcase oil.

Since the build-up of corrosive material is continuous, the problem cannot be solved by adding a neutralizing agent to the initial fill of oil, for it becomes exhausted.

Marine diesels are usually provided with a circulation system through which a portion of the oil is withdrawn from use, passed through a cleaning step and returned to use. There have been proposals to add to the oil, during cleaning, certain corrosion inhibitors or materials which will react with the corrosive materials and permit their removal when the oil is cleaned. These may work well with crankcase oil which is an ordinary hydrocarbon oil. However, the nature of the duty imposed upon crankcase lubricants has caused the provision of oils containing various additives, such as anti-oxidants, detergents, and the like, and the use of such oils, with cleaning systems of the usual type and using the usual cleaning reagents, would result in the removal or alteration of the additives, resulting in quick degradation of the lubricating ability of the crankcase oil.

This invention is directed to a solution of this problem and has for its principal object the provision of a method of lubricating the crankcase of an engine, which engine employs fuels tending to introduce strong mineral acids into the crankcase contents, with a crankcase oil which is cleaned by a method of cleaning which:

(1) Does not introduce into the oil metallic compounds capable of forming corrosive ash at high temperatures;

(2) Does not react with oxy-components of the oil to form soaps which render the oil emulsive, making it difficult to separate water from the oil in cleaning, and causing the formation of emulsions during use when, for example, entrained water is present;

(3) Does not alter, react with, remove or destroy useful additive components of the oil;

(4) Does not introduce into the oil components which may become altered under conditions of use and become damaging to the oil, to the engine, or to the circulating system.

All of these objects may be achieved by the practice

hereinafter described, as well as other objects and advantages which are developed hereinafter.

This invention is based upon the use, in cleaning of oils employed in the circulatory crankcase lubricating system of engines operating upon "sour" fuel oils, of a wash water containing certain alkaline earth metal salts.

Strongly basic materials, such as hydroxides of potassium and sodium, are frequently used in cleaning oils in circulating systems. It is difficult to exclude crankcase lubricating oil from the combustion chamber, and in many instances that oil is also used as cylinder lubricant. Residual fuels commonly contain vanadium. Combustion, where alkali metals are present, even to slight degree, and vanadium is also present, gives rise to an ash which may be extremely corrosive to metal parts. On the other hand, alkaline earth metals, notably calcium, are annocuous in this regard. Because of this, there is a growing practice of providing lubricants containing calcium based additives. Strongly basic materials, however, may tend to react with and to destroy calcium based additives. These two considerations rule out alkali metal as an active ingedient of cleaning agents, because of ash and because of deleterious effect upon additives.

Basic organic amines are useful from the ash forming standpoint, but many of these materials, such as morpholine or hydrazine, emit noxious fumes at the temperature involved, others give rise to emulsion difficulties, and some are toxic.

In operation of marine diesel engines on sour bunker fuel oil, a crankcase oil is withdrawn from the engine and washed with water. Following the water washing, the oil is separated from the water, e.g., by permitting the water to settle and removing the water phase, or by centrifuging. Then, the oil is returned to the crankcase lubrication system. The frequency of the washing or cleaning operation will vary, primarily, with the rate at which the acidic materials accumulate in the oil. In some cases this will mean almost continuous removal and cleaning and, in other cases, less frequent treatments. Water, alone, however is not effective to remove strong acids. Hence, a cleaning agent is required. As discussed hereinbefore, strongly basic materials and basic amines are not applicable.

The cleaning agents utilizable herein are aqueous solutions of certain water-soluble alkaline-earth metal salts of the lower fatty acids. The alkaline earth metal must have an atomic number of at least 20 and an atomic weight of at least 40, i.e., it will be barium, calcium, or strontium. The metal salt of the weak acid must be soluble in water, at least to the extent of about two percent. It has been found, however, that the formates tend to render the treated oil emulsive. Accordingly, the salts utilizable herein are salts of fatty acids containing 2 to 5 carbon atoms per molecule, i.e., the acetates, propionates, butyrates, and valerates (pentanoates) of barium, calcium, and strontium. The acetates, particularly calcium acetate, are preferred.

The concentration of the aforedescribed alkaline earth metal salt in the aqueous cleaning agent can vary from about 2 percent up to the limit of solubility in water, but in no case above about 25 percent. In practice the concentration will be between about 2 percent and about 10 percent. It will be appreciated that the amount of aqueous cleaning agent used must be at least sufficient to neutralize the strong acidity of the oil being treated. Thus, the amount of aqueous cleaning agent used will be between about 2 percent and about 15 percent, by volume, based upon the total volume of oil and aqueous treating agent.

In testing various reagents for this use, a used oil, containing strong acid resulting from combustion of a "sour" fuel was used. This oil was subjected to water

washing and to washing with water solutions of the various agents noted. The volume of water or aqueous solutions that was used was 5 percent by volume of the total volume of oil and water. The oil and the water or water solution were first vigorously mixed at a temperature of 180° F., and then the mixture was centrifuged in a continuous De Laval gyro-test unit. This was operated with the proper adjustable draw-off screw for the relative densities of the fluids, and the flow was throttled to the low rate of 50–100 cc. per minute to allow ample time for separation. Then the oil phase was separated and tests conducted thereon.

Strong acid number (S.A.N.), pH, and ash were determined in accordance with the usually accepted ASTM procedures D664–54 and D482–46. Emulsifying properties were evaluated according to Federal Standard Method 3201.5. The results are shown in the following Table I in which the concentrations of reagents are shown as percentage by weight in the water phase. In all the tables, the abbreviation, "Ac," signifies acetate. In lines 4 to 9, inclusive, and lines 14 to 18, inclusive, of Table I the reagent concentrations shown are equivalent in alkalinity to 1 percent NaOH.

not to an objectionable degree. However, at concentrations above 25 percent, the emulsive characteristics are too poor. It will also be noted that strontium and barium acetates (lines 14 and 15) are very effective and do not render the oil unduly emulsive. On the other hand, the magnesium salt (line 16) made the oil highly emulsive. Thus, the magnesium salts are not utilizable herein. Likewise, the alkaline earth metal salt of an acid other than fatty acids (line 17) and the lowest fatty acid salt, the formate (line 18) left the oil emulsive. Thus, these materials are not contemplated.

The object of removing strong acids, of course, is to prevent corrosion of engine parts by the oil. The corrosive tendencies were tested by placing 90 cc. of test oil and 10 cc. of distilled water in a bottle containing a weighed clean steel strip and a weighed clean copper strip. The bottle was sealed and rotated end over end for two weeks, at a temperature of 130° F. At the end of the test period, the sheets were reweighed. The corrosive tendencies of a fresh diesel crankcase oil containing detergent and anti-oxidant, of a used batch of this oil, and of a used batch treated with 10 percent aqueous calcium acetate solution were determined in this test.

Table I

Line No.	Reagent	Percent	pH	S.A.N.	Ash, percent	Emulstion Test—Sep'd. Layers after 30' at 180° F.		
						Oil, cc.	Water, cc.	Emulsion, cc.
1	Original Oil		3.0	0.10	0.05	33	4	43
2	Water		3.3	0.06		40	35	5
3	NaOH	1.0	6.2	Nil	0.05	10	6	64
4	Na_2CO_3	1.4	6.5	Nil	0.04			
5	$Na_3PO_4.12H_2O$	4.3	6.7	Nil	0.04	0	20	60
6	Triethanolamine	3.6	5.6	Nil		9	6	65
7	Morpholine	2.2	5.9	Nil		24	8	48
8	$Ca(Ac)_2.H_2O$	2.2	5.4	Nil	0.05	40	27	13
9	$Ba(OH)_2$	3.0	7.0	Nil	0.15	40	28	12
10	$Ca(OH)_2$	Sat.	3.0	0.06	0.02			
11	NaOH	12	10.1	Nil	0.26	0	0	80
12	Na_2CO_3	10	9.2	Nil	0.46	1	0	79
13	$Ca(Ac)_2.H_2O$	22	5.7	Nil	0.13	30	22	28
14	$Sr(Ac)_2.\frac{1}{2}H_2O$	2.7	5.5	Nil	0.07	40	40	0
15	$Ba(Ac)_2.H_2O$	3.4	6.0	Nil	0.09	25	37	18
16	$Mg(Ac)_2.4H_2O$	2.7	4.8	Nil	0.03	0	0	80
17	Calcium Lactate	2.7	4.6	Nil	0.03	29	8	43
18	Calcium Formate	1.6	4.8	Nil	0.03	27	5	56

It will be noted that water alone did not achieve great reduction of S.A.N. and that sodium hydroxide, the sodium phosphate compound, triethanolamine and morpholine all gave rise to emulsive oils (lines 3 to 7, inclusive) in addition to the known effects of residual sodium in the presence of vanadium from fuel ash (which objection applies to sodium carbonate as well), and that higher percentages of sodium hydroxide and sodium carbonate (lines 11, 12) increased this emulsibility trouble. Calmium hydroxide (line 10) used as saturated solution, gave no emulsion trouble, gave an innocuous ash, but did not, as used, give great reduction in S.A.N. Barium hydroxide (line 9), effected complete reduction of S.A.N., gave an innocuous ash and minor emulsion trouble, but barium hydroxide, unless completely removed, reacts with combustion gases or CO_2 in atmosphere to give insoluble barium carbonate which will collect in oil passages and the like, with adverse results.

Calcium acetate, both in relatively weak solution (line 8) and strong solution (line 13), effected complete reduction of S.A.N., gave an innocuous ash, and in the dilute, but competent, reagent of line 8 gave little emulsion trouble. At a higher concentration (line 13), calcium acetate rendered the oil somewhat emulsive, but

The results are compared in Table II.

Table II

Oil	pH	S.A.N.	Wt. Loss, mg.	
			Steel	Copper
New	7.3	Nil	5.2	13.0
Used	2.0	0.6	33.2	41.8
Used, treated with 10% $Ca(Ac)_2$	6.4	Nil	7.0	5.8

It will be noted that the treated oil is comparable to the new oil. Indeed, it appears to be less corrosive to copper than the new oil. The used oil, on the other hand, is highly corrosive to both metals.

Of importance is the effect upon additives in the oil treated. In a test upon a used oil containing an anti-oxidation additive, as reported in Table III below, the strong acid was removed and the treated oil was found not to have lost its additive-created stability. This table also contrasts the treatment with calcium acetate with treatment with a commercially available reagent recommended for this use, which contains sodium hydroxide and which is denoted in the table as "reagent S."

Table III

Reagent	Percent	Before Oxidation		After Oxidation	
		pH	S.A.N.	Increase in N.N.	Increase in Visc. at 210° F., Percent
Original oil		2.6	0.18	0.5	8.8
"Reagent S"	4.0	9.7	Nil	8.1	47.0
$Ca(Ac)_2.H_2O$	2.2	4.0	Nil	1.0	11.4

From the above, the essential parallelism of the oxidation results upon the original oil and the oil treated with calcium acetate shows that the oxidation inhibitor is still present and active after cleaning. Treating with "reagent S" rendered the oil very unstable.

The oxidation test used was one in which 25 cc. of oil are exposed to iron, copper, lead, and aluminum strips for a period of 40 hours at 260° F., while air is blown through the oil.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. That method for the lubrication of an internal combustion engine operating upon a "sour" fuel oil and contaminating its crankcase oil with strongly acidic substances which comprises withdrawing crankcase oil from the engine, washing that oil with an aqueous solution of a salt selected from the group consisting of the water-soluble barium, calcium, and strontium salts of fatty acids containing from 2 to 5 carbon atoms, inclusive, separating the wash reagent from the oil, and returning the cleaned oil to the crankcase.

2. The method of claim 1 in which the salt in the aqueous solution is an acetate.

3. The method of claim 1 in which the wash reagent is an aqueous solution of calcium acetate.

4. The method of claim 1 in which the wash reagent is an aqueous solution of barium acetate.

5. The method of claim 1 in which the wash reagent is an aqueous solution of strontium acetate.

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