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METHOD OF EXAMINING OIL SAMPLES

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This invention relates to a method of examining oil. More particularly, the invention relates to the examination of a lubricating oil which has been used in the crankcase of an internal combustion engine.

The present application is a continuation-in-part of an earlier filed copending application Serial No. 597,297, filed July 11, 1956, which is a continuation-in-part of Serial No. 275,956, filed March 11, 1952, which in turn is a continuation-in-part of Serial No. 793,331, filed December 22, 1947.

The object of this invention is to obtain information as to the condition of a lubricating oil and the engine in which the oil was used.

Another object is to determine the amount of fuel soots in the contaminants of a lubricating oil.

Other objects and advantages of the invention are apparent from the detailed description which follows:

Lubricating oils used in internal combustion engines are contaminated by many kinds of substances of varying particle mass. The nature of these substances or contaminants will vary with the type of engine, the fuel employed and the conditions under which the engine operates. In general, these contaminants are fuel soots; metal or metal oxide particles from either lead additives in the fuel or surfaces of the engine exposed to the oil or fuel; and oxidation products resulting from the combustion within the engine. Of course, foreign particles from the atmosphere may also become entrained in crankcase oil and be said to contaminate the oil.

It is believed that because of the numerous carboxyl, hydroxyl and keto groups in the molecular structure of the oxidation products, molecules of these products are mutually attractive. For the same reason, the oxidation products are also attracted to the particles of metal oxide and soot, forming coated particles which because of this mutual attractiveness of the oxidation products, tend to form larger masses from the smaller ones. The oxidation products may become linked to each other by primary valence bonds, in which case polymerization or an analogous chemical reaction takes place. Perhaps the more common phenomena which occurs is that the coated particles are attracted to each other by London-Van der Waals forces and become bound together only by secondary valence bonds.

Irrespective of how larger and larger particles are formed, it is well known that the particle size or mass of a contaminant is usually sub-microscopic when the contaminant first becomes entrained in the oil, and that the particle size increases until a point is reached where particles are formed of a sufficient mass to be recovered by merely diluting the oil with a thinner such as naphtha, petroleum ether or the like and centrifuging the diluted oil. The particles so precipitated and separated from the oil by centrifugal force are known as naphtha solids, and the amount of naphtha solids in a given quantity of oil may be readily observed following the separation.

The above described method of recovering a measurable quantity of naphtha solids from a sample of lubricating oil gives only very limited information concerning contamination in the oil and the condition of engine from which the sample is taken. For example, if an appreciable quantity of naphtha solids is observed, there is reason to suspect that the oil slots in the oil rings of the engine and the oil return holes in the pistons may be clogged.

However, there may be and usually is if naphtha solids are observed, a considerable and undetermined amount of contamination in smaller particle sizes.

Determination of some of the contaminants of smaller particle size than naphtha solids may be accomplished by a two-step process. First, the naphtha solids in a given sample are precipitated by dilution and recovered by centrifuging as described hereinabove. Second, a coagulant consisting of 98% by weight aniline and about 2% by weight water is added to the diluted sample which is then subjected to a second centrifuging. The second step causes some of the finer particles to coagulate and be deposited on top of the naphtha solids recovered in the first step. The difference in the amount of precipitate recovered in the first and second step is readily observed or measured and this difference which indicates the quantity of contaminants of smaller particle size than the naphtha solids, is denominated herein as the "sludge" index. Obviously, this process may also be carried out by treating two separate portions of the same sample, the first portion with a thinner only and the second portion with a thinner and the aniline-water coagulant, and the difference, if any, between the amount of precipitation is measured to determine "sludge" index.

A method has been discovered for separating and measuring the fuel soots from the total quantity of contaminants recovered from an oil sample taken from the crankcase of an internal combustion engine. A method has also been discovered detecting engine deposition by examining engine oils from railroad, stationary, marine, and similar diesel engines.

Manipulative procedure

This part of the detailed description of the invention will be in the form of a specific example.

5 ml. of an oil sample are placed in a 15 ml. graduated centrifuge tube. 8 ml. of naphtha thinner are added and the tube and its contents centrifuged in the conventional manner. The volume of naphtha solids so collected is directly observed or measured from the graduations on the tube. ½ ml. of a solution comprising 2% by weight of water and 98% by weight of aniline is then added to the centrifuge tube and the tube and its contents again centrifuged.

To a 5 ml. portion of a sample in a centrifuge tube is added 8 ml. of solvent naphtha and ¼ of one percent by volume of diphenylguanidine based on the 5 ml. of sample. The amount of diphenylguanidine so added is in the form of a 10% by weight solution in equal parts by volume of anhydrous ethyl alcohol and toluene. The tube and its contents are centrifuged and the volume of solids recovered is observed from the graduations on the centrifuge tube.

To a 5 ml. portion of a sample in a centrifuge tube, 1 ml. of N-butyl diethanolamine and 8 ml. of solvent naphtha are added. The tube and its contents are centrifuged, and the total volume of precipitated solids so recovered is measured. This is the NBD test.

The above-described coagulant N-butyl diethanolamine used in the invention may be added directly without dilution to another portion of the oil sample. About one part by volume of coagulant is added to about five parts by volume of sample. To this mixture is also added about seven or eight parts by volume of a thinner, such as naphtha or petroleum ether, whereupon the coagulated contaminants in the sample are quantitatively recovered by centrifuging. The same relative volume of coagulant diluted with a lower alkyl alcohol or alcohol and water may also be employed. Methyl and ethyl alcohol are preferred diluents since they have some coagulating effect on contaminant particles "held" by a detergent additive. Other alcohols, however, may be used including n-pro-

panol, isopropanol, N-butanol and isobutanol. As much as two parts by volume of water may be added to one part of alcohol, if it is desired to mix the alcohol diluent with water. The solution of coagulant in alcohol or alcohol and water should contain from about 0.2% to 2.0% by weight of the N-butyl diethanolamine.

A considerable amount of uncoated fuel soots is often found in the used oil from an automotive diesel engine. These soots are precipitated by the aniline-water coagulant used to determine sludge index and will indicate a very high reading of sludge if not removed. It was found that fuel soots are floated off from the sludge index precipitate by carbon tetrachloride, leaving the naphtha solids and particles coagulated by the aniline-water mixture. To accomplish this separation, carbon tetrachloride is added to the centrifuge tube at the conclusion of the sludge index test and the soots which tend to float on top of the carbon tetrachloride are decanted off. The volume of precipitate left then may be read against the graduations of the centrifuge tube. The quantity of fuel soots may also be determined by subtracting the volume of precipitate after removal of soots from the volume before removal. Alternatively, the dry weight of the fuel soots may be measured by drying and weighing the soots floated off by the carbon tetrachloride. The fuel soots may also be removed after the DPG test or the NBD test if desired. An illustrative example of the effect of fuel soots on sludge index readings is as follows (readings are percentage by volume):

	Naphtha Solids	Sludge Index	DPG Test	NBD Test
A	0.2	10.0	14.0	16.0
B	0.2	0.3	14.0	16.0

In series A of the above example, the fuel soots were not removed, and in series B they were removed after the sludge index test. The engine from which the sample for this example was taken was in fairly good condition for an automotive diesel engine, but without removing the fuel soots from the sludge index precipitate, considerable deposits in the engine would be indicated.

Another aspect of the invention relates to oil samples from stationary railroad, marine and similar diesel engines which, as stated above, are usually quite clean. It was discovered that if the NBD test alone is performed on these samples, preferably using both alcohol and water with the coagulant, whether or not there is deposition in the engine is determined by a simple manipulation of the centrifuge tube and its contents after the NBD test is completed by centrifuging. This manipulation comprises inverting the tube and observing the behavior of the precipitate. If the precipitate falls out and becomes dispersed in the liquid below, no engine deposits are likely to be present. On the other hand, if the precipitate does not fall out and become dispersed in the liquid, engine deposits are indicated which are commensurate in extent with the volume of precipitate. The presence of detergent additives is also determined by this test when the sample is relatively clean and water is employed with the coagulant, since the precipitate will become cloudy if a detergent is present and form soft curds which are emulsions of the water and the detergent.

The above-described illustrations and examples are not to be construed as limiting the scope and spirit of the invention except as it is defined in the appended claims.

What is claimed is:

1. The method of examining engine oils from railroad, stationary, marine and similar diesel engines to detect engine deposition, comprising adding to an oil sample a thinner and a coagulant consisting essentially of N-butyl diethanolamine, centrifuging to precipitate solids, and then inverting the centrifuge tube and its contents, the failure of the precipitated solids to fall out of the tube indicating that engine deposition is occurring.

2. The method of claim 1 in which the coagulant comprises a solution containing water, methyl alcohol, and N-butyl diethanolamine.

3. The method of claim 1 in which the coagulant comprises a mixture of ethyl alcohol and N-butyl diethanolamine.

4. In a method of examining oils from automotive and similar diesel engines to determine engine deposition where solids are precipitated from an oil sample by adding a thinner and an aniline-water mixture to the sample and centrifuging to recover a measurable quantity of solids, the improvement which comprises removing the fuel soots from said solids by floatation with carbon tetrachloride.

5. In a method of examining oils from automotive and similar diesel engines to determine engine deposition where solids are precipitated from an oil sample by adding diphenylguanidine to the sample and centrifuging to recover a measurable quantity of solids, the improvement which comprises removing the fuel soots from said solids by floatation with carbon tetrachloride.

6. In a method of examining oils from automotive and similar diesel engines to determine engine deposition where solids are precipitated from an oil sample by adding N-butyl diethanolamine to the sample and centrifuging to recover a measurable quantity of solids, the improvement which comprises removing the fuel soots from said solids by floatation with carbon tetrachloride.

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