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METHOD OF OIL TESTING AND COMPOSITION THEREFOR

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The present invention relates to an acid-base indicator composition for the testing of lubricating oils and particularly for the determination of the time at which the concentration of acidic contaminants in used lubricating oil has risen to a value such that the oil should be replaced. It also relates to a method of applying such a composition to a used lubricating oil and determining the characteristics of the oil.

It is well known that during use in internal combustion engines crankcase lubricating oil gradually becomes contaminated with acidic materials. These acidic materials are primarily derived from the products of combustion of the fuel used in the engine. When the concentration of these contaminants in the oil rises above a certain value the oil becomes acidic, the wear in the engine increases rapidly and the life of the engine is thereby greatly shortened.

Relatively recent developments in the lubricating oil art have included the discovery of additives which impart to the oil a much greater capacity for absorbing or neutralizing acidic contaminants before the oil itself becomes acidic. However, the protection afforded by a given concentration of any of these additives is inherently limited and there comes the inevitable time at which the protection is exhausted. Unless the used oil is replaced shortly thereafter by new oil, the engine wear-rate will rapidly increase. The net effect, then, of the so-called anti-acid additives is merely to postpone the point at which the oil becomes acidic and thus development of acidity still remains the most usual limitation to the useful life of a given "fill" of crankcase lubricating oil, especially in "stop-and-go" driving and in cold weather. Therefore, the problem of determining the point at which the oil should be replaced has remained a serious problem, for if this point is not correctly determined the benefits of the anti-acid additives will be lost.

The determination of the acidity which has developed in a used lubricating oil has long been a difficult problem. Classical color indicator titration or spot testing techniques have failed to give satisfactory results because it is usually impossible to detect the indicator color in the oil. The colored constituents of the used oil, particularly the dispersed semi-solid or solid carbonaceous materials, are black and interfere with or mask the color of the indicator. Modern laboratory techniques now involve the use of potentiometric titration and thus avoid the necessity of detecting a color change in an oil sample. However, this method is of limited application because the apparatus is expensive and the technique requires specially trained personnel. It is usually employed only when a thorough study of the oil is to be made under laboratory conditions. The average motorist or automotive fleet operator does not have a laboratory or trained personnel at his disposal, and, heretofore, it has been the standard practice to change crankcase oil at regular intervals based on mileage. However, automotive equipment is generally operated under widely varying conditions; therefore, even the conscientious operator may often change

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his oil either before he needs to or not until after the oil has become so acidic as to harm the engine.

It is therefore a principal object of the present invention to provide an acid-base indicator composition by the use of which one can simply, quickly and inexpensively determine whether a used crankcase lubricating oil is suitable for further use in an internal combustion engine. A further object is to provide an acid-base indicator composition the application of which to accomplish this purpose requires no training in laboratory techniques. Another object is to provide an indicator composition which, when applied according to the method of the invention, will indicate whether a used lubricating oil has become too acidic for continued use by the development of a clear and distinct color regardless of the presence of black carbonaceous material dispersed therein. A still further object of the invention is to provide a method for the application of such an acid-base indicator composition to the used lubricating oil. Other objects will be apparent in the following description and discussion of the invention.

In accordance with the present invention, it has been found that the determination of the suitability of a used crankcase lubricating oil for further use in an internal combustion engine may readily be made by contacting said oil and an acid-base color indicator on a thin porous medium in the presence of an essentially neutral solution, hereinafter to be called a "developer solution," which comprises a substantial proportion of a liquid oxygenated organic compound and water whereby the oil, indicator and developer solution migrate through said medium in a direction parallel to its surface.

In order to elucidate the invention, the following specific example will be given of its application. This is a preferred embodiment of the invention but is not to be considered a limitation thereof.

A drop of oil is transferred from the dip-stick of an automobile engine to a piece of Whatman's No. 4 filter paper. A small quantity, in the order of a few drops, for example, from 1 to 20 drops, of the indicator-developer solution described below is poured from an eye-dropper over the drop of oil. The oil and indicator-developer solution commingle and the resulting solution migrates outwardly from the original position of the drop of oil. The dispersed black carbonaceous solid or semi-solid material in the used oil is left at the original position of the drop of oil. The migrating solution of oil and indicator-developer solution is therefore of a light color and transparent. Within a few seconds, a colored ring will develop, surrounding the original position of the drop of oil but outwardly and apart therefrom. A red ring indicates that the oil is acidic and should be discarded; a green ring indicates that the oil is still suitable for continued use; an indistinct or yellowish color indicates that the necessity for discharging the oil is imminent. This is the entire extent of the necessary manipulation and interpretation by the person making the test. It is readily apparent that the test is extremely simple and quick; no laboratory equipment is involved, and the results are easily interpreted.

The indicator-developer solution used in this example is of the following composition, and is a preferred embodiment of one aspect of the invention:

Developer solution

	Percent by volume
Ethanol (containing 5% v. water)-----	32.0
4-methyl-2-pentanol -----	17.0
Petroleum solvent (about 65% w. aromatics, approx. boiling range, 238 to 312° F.)-----	25.2
α -methyl-naphthalene -----	25.0
Glycerol -----	0.8

Indicator dissolved in above developer solution

Bromocresol green.....	57 mg./100 cc. of solution.
Naphthyl red (S. A.) (4-amino-1-naphthaleneazobenzene-4'-sulphonic acid).....	67 mg./100 cc. of solution.

Inorganic base to adjust indicator-developer solution to neutrality

Sodium hydroxide in ethanol (0.1 normal).....	To neutrality (about 0.8 ml.).
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An illustration of the applicability and dependability of the present invention is as follows: The above-exemplified indicator-developer solution composition and method were applied to a crankcase lubricating oil in normal passenger car service over an extended road test without oil make-up. The lubricant was a solvent refined petroleum oil of SAE 30 viscosity and contained a sufficient amount of calcium petroleum sulfonate and calcium salt of the condensation product of octylphenol with formaldehyde such that its sulfated ash amounted to 0.4% by weight. The following data were obtained:

Miles of Driving.....	0	750	1,600
Indicator Test of Present Invention:			
Color of Ring.....	Green	Green	Red
pH of Oil by Potentiometric Titration.....	9.5	6.0	4.0
Base No. of Oil, mg. KOH/gm.....	2.5	0.6	0.0

It is apparent from the above data that at 750 miles the oil still contained alkaline material and was suitable for further use, although its reserve alkalinity had been considerably reduced. At 1600 miles the alkalinity had become exhausted, the pH of the oil had dropped to a point of increasingly high wear rates and the oil was no longer suitable for further use. The test of the present invention clearly indicated the suitability of the oil for further use at 750 miles and the necessity of an oil change at 1600 miles. It is obvious from this that the composition and method of the present invention are of great utility to persons who desire to, or must, make the decision whether to change oil without the benefit of laboratory services.

The method of manipulating the test materials can be varied extensively. It is immaterial to the invention whether the oil is first placed on the porous medium and thereafter the indicator-developer solution is applied, or whether the indicator is first applied to the porous medium in dry or solution form, and then the oil drop and developer solution are successively applied. It is preferred that the application of the developer solution follow the application of the oil drop and follow or coincide with the application of the indicator, but the method is operable even if the oil is applied after the wetting of the medium with the developer solution. Any quantity of developer solution can be used as long as it does not wash all of the oil off the porous medium. Thus, as little as 1 drop can be used or as much as even 25 or 50 cc. Economic considerations will ordinarily preclude the use of more than 1 to 2 cc.

The porous media which are suitable for the purposes of the invention are sheet-like masses having uniform adsorptive properties and which are a light or white color and are substantially neutral to the indicator used. By a "sheet-like" mass is meant one which has a thickness no greater than 1 to 2 millimeters and which has on one side a boundary surface area of at least 4 square centimeters. The medium can be either a fibrous or granular material. Fibrous material so interlocked as to be self-supporting is ordinarily preferred; however, loose fibrous or granular materials which must be supported by another medium are fully operable and may even be preferred in some circumstances, as will be evident to anyone concerned with the practicing of the invention. Examples of porous media which are self-supporting fibrous sheet-like masses are unglazed paper and cloth. A particularly preferred

material in this class is an analytical filter paper, such as Whatman's No. 4, No. 2, or No. 1. In general any commercially available analytical filter paper will give excellent results. If the material is cloth, it is preferred that it be a cellulose type such as cotton. Examples of porous media which are not self-supporting are uncalendered loose cellulose fibers and gels such as a neutral magnesia silica gel. This type of material can be spread in a thin layer on any convenient non-porous supporting medium such as cellophane, glass, metal or the like, and subsequently used in the same manner as the above-mentioned paper or cloth.

Indicators which are suitable for practicing the invention are any of the well known organic acid-base indicator compounds or any combination thereof, which changes color in a desired pH range. Preferred indicators are those which develop strong colors, are stable in air for at least one or two minutes, and are not sensitive to short exposures to the small atmospheric concentrations of carbon dioxide.

Examples of specific preferred indicators are bromophenol blue, bromochlorophenol blue, paraethoxycrysoidine, bromocresol green, methyl red, bromocresol purple, bromothymol blue, quinoline blue, naphthyl red (4-amino-1-naphthaleneazobenzene), naphthyl red (S. A.) (4-amino-1-naphthaleneazobenzene-4'-sulfonic acid) or salt thereof, and many others.

As indicated above, there are two distinct compounds which are frequently referred to as naphthyl red, one being the sulfonic acid derivative, or salt thereof, of the other. In order to distinguish between the two we choose to call the parent compound "naphthyl red" and the sulfonic acid derivative, or salt thereof, "naphthyl red (S. A.)." Various chemical names have been given in the literature to the compound "naphthyl red," depending upon the system of nomenclature used—for example: benzeneazo- α -naphthylamine (Clark, "The Determination of Hydrogen Ions," 3rd ed., p. 78, Baltimore, The Williams and Wilkins Company, 1928), 4-benzeneazo-1-naphthylamine or 4-phenylazo-1-naphthylamine (Eastman Organic Chemicals, List No. 38, pp. 28, 163, Rochester, Distillation Products Industries, 1952). We prefer the name 4-amino-1-naphthaleneazobenzene in accordance with the Chemical Abstracts system (Introduction to the 1945 C. A. Subject Index, p. 5917). Similarly, various names have been given to the compound "naphthyl red (S. A.)," or salt thereof—for example: p-benzenesulfonic acid-azo- α -naphthylamine (Clark, supra, p. 78), α -naphthylamine-azobenzene-p-sodium sulfonate (Catalog No. 26, Laboratory Chemicals, p. 93 (No. B151), East Rutherford, N. J., Matheson Coleman and Bell, Inc., 1953). Again, we prefer the name in accordance with the C. A. system, viz., 4-amino-1-naphthaleneazobenzene-4'-sulfonic acid.

The particular pH range which is selected for the color change is immaterial to the present invention. However, the most usual range which will be selected is one somewhere between 3 and 6. It has been found that the wear rate in an internal combustion engine most frequently rises sharply when the crankcase oil approaches the neighborhood of a pH range of 4 to 5, and therefore particularly preferred indicators for the practice of the invention are those which exhibit a color change in that pH range.

Although a single suitable indicator compound is completely satisfactory, it is often preferred to use a combination of two or more compounds. For example, by a suitable selection of compounds it is possible to obtain the colors red and green to indicate, respectively, acid (dangerous) and basic (safe) oils. Examples of such preferred combinations are (1) naphthyl red (S. A.) and bromocresol green, (2) naphthyl red (S. A.) and bromophenol blue, (3) naphthyl red and bromocresol green, (4) naphthyl red (S. A.) and bromochlorophenol blue, (5) p-ethoxycrysoidine and bromocresol green, and others.

If the indicator is to be applied to the porous medium before either the oil or the developer solution, its concentration on the surface thereof should ordinarily be at least 0.05, but preferably greater than 0.2, milligram per square centimeter of surface. Much higher concentrations than this are operable, however, even up to 10 or 20 milligrams per square centimeter of surface. A maximum of 5 milligrams per square centimeter of surface will give best results. These concentrations can be doubled in the case of a combination of two indicator compounds or tripled in the case of a combination of three, etc.

If the indicator is to be incorporated into the developer solution and applied to the oil drop therewith, its concentration should be at least 0.0001, and preferably at least 0.0004, gram mole per liter of developer solution. Higher concentrations than these are operable and often desirable. In the case of the indicators of relatively low intensity colors, as high a concentration as 0.05 gram mole per liter can be used to advantage. It is preferred, however, that no more than 0.02 gram mole per liter be incorporated into the developer solution. When two or more indicator compounds are used the concentration of each can be as above. In the specific case of the combination of naphthyl red (S. A.) (m. w. 327) and bromocresol green (m. w. 698) especially effective concentrations are 0.001 to 0.004 gram mole of naphthyl red (S. A.) and 0.0004 to 0.0016 gram mole of bromocresol green per liter of developer solution, and particularly preferred ranges are 0.0016 to 0.0024 gram mole of naphthyl red (S. A.) and 0.0006 to 0.0010 gram mole of bromocresol green per liter of developer solution.

The basic functions of the developer solution are to dissolve the oil and indicator, to provide sufficient water for the ionization of the acid constituents and to effect migration of the oil and indicator through the porous medium whereby the black carbonaceous material dispersed in the original oil is separated from the oil and indicator. It has been discovered that a suitable solvent to accomplish these functions is one which comprises a solution of a small amount (in the order of from about 0.5 to about 20% v.) of water in an essentially neutral liquid oxygenated organic compound. The developer solution must be essentially neutral to the indicator used and to this end it is occasionally necessary to adjust it to neutrality by the incorporation therein of a small amount of inorganic base. A suitable base for this purpose is sodium hydroxide dissolved in ethanol, and a 0.1 normal solution thereof is convenient. Ordinarily only about 0.1 to 2% v. of this 0.1 normal solution need be used because the preferred components of the developer solution are inherently neutral and any acidity present will be due to impurities only. The developer solution must have a sufficiently low viscosity to effect the migration of the oil and indicator through the porous medium. Thus the viscosity must not be higher than about 20 centipoises at 100° F., and preferably no greater than 10 centipoises at 100° F. Particularly good results will be obtained if the viscosity of the developer solution is not greater than 3 centipoises at 100° F.

The "liquid oxygenated organic compound" can be any one or a combination of such compounds which have the following characteristics:

1. Ability to retain in solution at least 0.5% v. of water,
2. At least substantial solvency for both water and hydrocarbons,
3. Substantial neutrality to the indicator used, and
4. Viscosity sufficiently low that the viscosity of the developer solution containing all of the components will not exceed the values specified above.

Specific examples of suitable compounds which meet these criteria are: Monohydroxy alkanols such as methanol, ethanol, isopropanol, n-propanol, n-butanol, tertiary

butanol, n-hexanol, cyclohexanol, fusel oil, secondary butanol, furfuryl alcohol, 2-ethylbutanol, ethylene chlorohydrin (2-chloroethanol), etc., aldehydes such as acetaldehyde, paraldehyde, butyraldehyde, furfural, benzaldehyde, crotonaldehyde, etc., alkanones such as acetone, methyl ethyl ketone, 2-hexanone, 4-methyl-2-pentanone, 2-pentanone, 2-heptanone, cyclohexanone, cyclopentanone, etc., ethers such as ethyl ether, esters such as methyl formate, ethyl formate, methyl acetate, ethyl acetate, isopropyl acetate, n-butyl acetate, secondary butyl acetate, isobutyl acetate, tert. amyl acetate, secondary amyl acetate, ethyl propionate, methyl lactate, ethyl lactate, etc. Of the many operable compounds or combinations thereof, it is preferred to use the oxygenated hydrocarbons. Particularly good results will be obtained with those aliphatic mono-functional alcohols, aldehydes, ketones, and esters which contain no more than 8 carbon atoms and preferably no more than 6 carbon atoms. Best results will be obtained with monohydroxy aliphatic unsubstituted alcohols containing no more than 4 carbon atoms.

The concentrations of the "liquid oxygenated organic compound" may be varied extensively. As noted above this may be the only component, other than water, in the developer solution and therefore its concentration can successfully be as high as 99.5% v. On the other hand it is often desirable to incorporate other components into the developer solution, as will be explained later, and in such a case, the concentration of the "liquid oxygenated organic compound" in the developer solution can be as low as 15% v. In general, it is preferred that the concentration be at least 25% v. and especially at least 30% v. A particularly effective composition of the developer solution is one wherein the concentration of the "liquid oxygenated organic compound" is from about 20 to about 40% v.

The addition of a water immiscible oil-solvent, especially an additional solvent mixture, will hasten a development of the indicator color during the test. It is preferred that this component, herein referred to as a "water immiscible oil-solvent" or a "solvent mixture," have an aromatic content of from 30 to 70% w., the remainder being non-aromatic hydrocarbons, such as paraffins and naphthenes. The aromatic content material can be monocyclic, dicyclic or poly-cyclic and may contain substituent groups such as chlorine. A petroleum fraction containing xylenes and non-aromatics of approximately the same boiling range is a particularly preferred material for this component, but the boiling range can be between about 100° F. and 400° F. The concentration of this component in the developer solution should generally be no higher than 70% v. or preferably 50% v. It is preferred that it be at least 4% v. A particularly effective concentration range is from about 15 to about 35% v.

It has also been discovered that an additional component may sometimes be desirable to sharpen the color change and make the color rings more distinct. Under some circumstances, certain lubricating oil additives such as calcium petroleum sulfonates may undergo a disproportionation reaction whereby, for example, calcium hydroxide and petroleum sulfonic acids are formed. When this occurs, these compounds may migrate at slightly different rates through the porous medium and this will lessen the distinctness of the color rings. To avoid this, it has been found that compounds such as glycerol, 1,2-propanediol, 1,4-butanediol, 1,2,3-butanetriol, erythritol, etc., may be added. The operable compounds for this purpose are defined as polyhydroxy alcohols having molecular weights no greater than about 160. It is only necessary to use a small proportion of this component. In some cases 0.1% v. based on the developer solution is sufficient, although generally at least 0.5% v. should be used. A preferred range is from about 0.8 to about 1.0% v. The concentration of this component should

not be greater than about 2.0% v. and preferably not greater than 1.5% v. to avoid any possible tendency for the development of a grey background color during the test.

Depending upon the composition of the developer solution, it may be desirable to add a solubilizing agent to insure that the polyhydroxy alcohol will be dissolved in the rest of the developer solution and will not be precipitated by the lubricating oil. This component is defined as an essentially neutral substituted aromatic compound having a boiling point of at least 150° C. It will be noted that this material can be substituted in whole or in part for the aromatic content of the above described solvent mixture. Examples of such suitable solubilizing agents are alpha-methyl-naphthalene and orthodichlorobenzene. This component has another advantageous function. It is high-boiling and therefore slow to evaporate and consequently prevents the development of a grey background color in the porous medium, which might occasionally occur, when ambient temperatures are high, as a result of precipitation of some of the solid indicator in the medium on evaporation of part of the solvent mixture. The concentration of this component in the developer solution should generally be no higher than 50% v. It is preferred that it be at least 4% v. A particularly effective concentration range is from about 15 to about 35% v.

One other component, which has been found to preserve the color of the indicator for a longer time after its development in the porous medium and also to maintain the color intensity of the indicator, is a high boiling (about 125° C., or above) monohydric alkyl, alicyclic or aryl alcohol. Methylisobutyl carbinol (4-methyl-2-pentanol) is a particularly preferred example of this component. If the above-defined liquid oxygenated organic compound is such an alcohol, there is of course no necessity for adding another. The concentration of this component can be varied extensively. If it is also to serve the function of the "liquid oxygenated organic compound," defined above, the concentration can be as high as 99.5% v. of the developer solution. If it is a separate and additional component, it is preferred that its concentration be at least 5% v. When the "liquid oxygenated organic compound" is a non-alcoholic compound or low molecular weight alcohol, a particularly suitable range of concentration of the present component is from about 10 to about 30% v.

The present invention is applicable to all commercially available lubricating oils which are suitable for use in internal combustion engines and which have viscosities in the range of from about 30 to about 500 Saybolt Universal seconds at 210° F. It can be successfully and advantageously applied to oils containing any of the common additives such as anti-acid additives, detergents, pour point depressants, viscosity index improvers, anti-oxidants, anti-foam agents, oiliness or film strength agents, etc. The anti-acid additives, as previously mentioned, are added to lubricating oils to provide reserve basicity whereby acidic contaminants are neutralized until the additive is exhausted. Most of these additives are also effective detergents and some are also anti-oxidants. Among such common anti-acid additives may be mentioned alkaline earth metal petroleum sulfonates, e. g., basic calcium, barium and magnesium sulfonates; oil-soluble phenate salts which by hydrolysis give rise to basic conditions, such as the oil-soluble polyvalent metal alkylphenates and particularly alkaline earth metal alkylphenates, e. g., calcium cetylphenate; alkylphenate-aldehyde condensation products, e. g., calcium and barium salts of condensation products of octylphenol and formaldehyde containing such as of the order of 5 phenol units per molecule; alkylphenate-sulfides, such as calcium and barium salts of condensation products of octylphenol and sulfur chloride, e. g., barium dioctylphenate mono- and di-sulfides (barium salt of dioctylphenol mono- or di-

sulfide); oil-soluble polyvalent metal alcoholates which by hydrolysis provide an alkaline condition, e. g., calcium octadecylate and calcium cetylale; basic alkaline earth metal alkylsalicylates such as basic calcium octylsalicylate; synthetic sulfonate salts such as basic barium salt of wax substituted naphthalene. Common detergents having a lesser anti-acid action but which are often present in lubricating oils include the aluminum naphthenates, alkaline earth metal phenyl stearates, and wax substituted naphthol-carboxylates and wax substituted phenol-carboxylate sulfides. Common pour point depressants include complex condensation products of paraffin wax and naphthalene or phenol, and methacrylate ester polymers, e. g., "Paraflow," "Santopour," "Acryloid." Common viscosity index improvers include butene polymers such as "Paratone," methacrylate ester polymers such as "Santodex." Common anti-oxidants, not already mentioned as anti-acid additives or detergents, include oil-soluble organo-sulfur and organo-phosphorus compounds such as sulfurized sperm oil, sulfurized oleic acid, sulfurized and/or phosphorized terpenes, lecithin, calcium cetyl phosphate, zinc dicyclohexyl dithiophosphate, and amines and phenol derivatives such as N,N'-tetramethyldiaminodiphenylmethane and alizarin. Anti-foam agents include polymethylsiloxanes, etc. Oiliness or film strength agents include phosphorus and/or sulfur containing compounds such as tributyl phosphite.

We claim as our invention:

1. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of an organic acid-base indicator compound which exhibits a color change in the pH range of 3 to 6 in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol and from about 4 to about 70% by volume of a homogeneous solvent mixture the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture, the concentration of said acid-base indicator compound in said developer solution being from about 0.0001 to about 0.05 gram moles of said indicator compound per liter of said developer solution.

2. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of an organic acid-base indicator compound which exhibits a color change in the pH range of 3 to 6 in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol, from about 0.1 to about 2% by volume of a polyhydroxy alcohol the molecular weight of which is no greater than about 160 and from about 4 to about 70% by volume of a homogeneous solvent mixture the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture, the concentration of said acid-base indicator compound in said developer solution being from about 0.0001 to about 0.05 gram moles of said indicator compound per liter of said developer solution.

3. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of an organic acid-base indicator compound which exhibits a color change in the pH range of 3 to 6 in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol, from about 0.1 to about 2% by volume of a polyhydroxy alcohol the molecular weight of which is no greater than about 160 and from about 4 to about 70% by volume of a homogeneous solvent mixture the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture, said developer

solution also containing a substantial proportion of an essentially neutral substituted aromatic compound which has a boiling point of at least 150° C., the concentration of said acid-base indicator compound in said developer solution being from about 0.0001 to about 0.05 gram moles of said indicator compound per liter of said developer solution.

4. An acid-base indicator composition which comprises from about 0.001 to about 0.002 mole of bromocresol green and from about 0.0002 to about 0.04 mole of 4-amino-1-naphthaleneazobenzene-4'-sulfonic acid per liter of a developer solution consisting essentially of from about 20% to about 40% by volume of aqueous ethanol containing from 0.5 to 20% by volume water based on said aqueous ethanol, from about 10% to about 30% by volume 4-methyl-2-pentanol, from about 0.1 to 1.5% by volume glycerol, from about 4% to about 70% by volume alpha-methylnaphthalene and from about 4 to about 50 percent by volume of a homogeneous solvent mixture which boils within the range of about 100° to about 400° F., and the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture.

5. The method for determining the suitability of a used lubricating oil for further use in an internal combustion engine which comprises contacting a small portion of said oil and an organic acid-base color indicator compound which exhibits a color change in the pH range of 3 to 6 in a thin light (in color) porous medium in the presence of an essentially neutral developer solution comprising essentially from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol, and from about 4 to about 70% by volume of a water immiscible oil-solvent.

6. A method according to claim 5 wherein the oil is contacted with a combination of two organic acid-base indicator compounds which is a mixture of bromocresol green and 4-amino-1-naphthaleneazobenzene-4'-sulfonic acid.

7. A method according to claim 5 wherein the developer solution comprises water, a monohydroxy alcohol, a polyhydroxy alcohol the molecular weight of which is no greater than 152 and a solvent mixture the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture.

8. A method according to claim 5 wherein the porous medium is filter paper.

9. The method for determining the suitability of a used lubricating oil for further use in an internal combustion engine which comprises placing a small quantity of said oil in a thin essentially white porous medium, pouring over said small quantity of oil a solution of an organic acid-base indicator compound which exhibits a color change in the pH range of 3 to 6 in an essentially neutral developer solution comprising essentially from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydric alcohol and from about 4 to about 70% of a water immiscible oil-solvent, the concentration of said acid-base indicator compound in said developer solution

being from about 0.0001 to about 0.05 gram moles of said indicator compound per liter of said developer solution.

10. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of an organic acid-base indicator compound which exhibits a color change in the pH range of 3 to 6 in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol and from about 4 to about 70% by volume of a water immiscible oil-solvent, the concentration of said acid-base indicator compound in said developer solution being from about 0.0001 to about 0.05 gram mole of said indicator compound per liter of said developer solution.

11. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of two acid base indicator compounds, one being bromocresol green and the other being a 4-amino-1-naphthaleneazobenzene compound having no substituents other than a sulfonic acid group in the 4' position, in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol, from about 0.1 to about 2% by volume of a polyhydroxy alcohol the molecular weight of which is no greater than about 160, and from about 4 to 70% by volume of a homogeneous solvent mixture the aromatic content of which is from about 30% to about 70% by weight of said solvent mixture, said developer solution also containing a substantial proportion of an essentially neutral substituted aromatic compound which has a boiling point of at least 150° C., the concentration of each of said acid-base indicator compounds in said developer solution being from about 0.0001 to about 0.05 gram mole per liter of said developer solution.

12. An acid-base indicator composition for the determination of the suitability of a lubricating oil for further use in an internal combustion engine which consists essentially of a solution of two organic acid-base indicator compounds, one being bromocresol green and the other being 4-amino-1-naphthalene-azobenzene, in an essentially neutral developer solution consisting essentially of from about 0.5 to about 20% by volume of water, at least 15% by volume of a monohydroxy alcohol and from about 4 to about 70% by volume of a homogeneous solvent mixture the aromatic content of which is from about 30% to 70% by weight of said solvent mixture, the concentration of each of said acid-base indicator compounds in said developer being from about 0.0001 to about 0.05 gram mol per liter of said developer solution.

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