INDICATING LUBRICANT ADDITIVE

Inventors: Sarah M. Cooper, Mountain View, CA (US); Michael Weiner, Webster, NY (US); Stuart G. MacDonald, Pultneyville, NY (US)

Correspondence Address:
Michael L. Weiner
Technology Innovations
Suite 215
150 Lucius Gordon Drive
West Henrietta, NY 14586 (US)

Appl. No.: 11/013,821
Filed: Dec. 16, 2004

Publication Classification

Int. Cl.
C10M 125/04 (2006.01)

U.S. Cl. 508/150; 508/551; 508/554

ABSTRACT

An indicating lubricant additive comprising a color-changeable polymer having an outer layer of a first color, and an intermediate layer of a second color; and a lubricant sensing dipstick comprising a circuit housing, an elongated body having a proximal end and a distal end, and lubricant sensing means disposed at said distal end, wherein in one embodiment, the sensing means detects a change in the indicating lubricant additive that is present in a lubricant.
INDICATING LUBRICANT ADDITIVE

[0001] This invention relates in one embodiment to a lubricant additive composition, and more particularly to an additive which changes in appearance in a manner that correlates with the lubricating properties of the lubricant through which it is distributed, and that results in a change in appearance in the overall lubricant-additive mixture.

FIELD OF THE INVENTION

[0002] A lubricant additive composition which changes in appearance in a manner that correlates with the lubricating properties or aging of the lubricant through which it is distributed.

BACKGROUND OF THE INVENTION

[0003] The use of viscous liquids and semi-solids (e.g., greases) as lubricants disposed between surfaces in motion at different velocities is well known and widely used. Such lubricants are used in particular in a variety of known mechanical apparatus, such as internal combustion (IC) engines, transmissions, electric motors, machine tools, and the like. The difference in velocities of the surfaces may be with respect to magnitude, direction, or both.

[0004] In some uses, the lubricant is used to prevent or significantly reduce wear and heat generation between the surfaces in motion, such as in bearings, piston rings, piston skirts, and gear teeth. Such surfaces may be engaged in rolling motion such as in the balls or rollers of a multi-race bearing, or in sliding motion such as in the shell bearings at the main and rod journals of a crankshaft in an automotive engine, or in the engagement of gear teeth.

[0005] In other instances, the lubricant is used to control the wear or cutting action and the heat generation between the surfaces in motion, particularly the action of a first surface or edge upon a second surface, such that a portion of the second surface is removed while essentially none of the first surface is removed. One example of such an application is the use of cutting fluids in the fabrication of parts using machine tools. Such fabrication may entail bulk cutting such as with the use of surface mills or lathe, the cutting action typically occurring at a highly localized region, such as at the cutting edge of a tool bit. Alternatively, such fabrication may entail the polishing of high precision surfaces such as optics, injection molds, and the like, the polishing action occurring in a somewhat localized region, or over a broad region depending upon the particular process and apparatus.

[0006] In both instances, control of the lubricant properties in order to achieve the desired end result is essential. In the case of wear prevention, the lubricant is used to prevent the occurrence of surface-to-surface contact between the surfaces in motion. In the case of surface removal, the lubricant is used to control the extent of surface-to-surface contact between the surfaces in motion. On a microscopic scale, the lubricant is subjected to an extremely high amount of shear, and possibly a high pressure, in the regions where the surfaces in motion are nearly in contact. In the case of surface removal, where locally there is surface-to-surface contact, lubricant molecules may be subjected to attrition and actual breaking of chemical bonds in the molecules at the point of such contact.

[0007] Much effort has been expended in order to make the bulk properties of lubricants robust to the effects of shear and attrition, and to the effects of other environmental conditions such as ambient or operating temperature, and localized adverse phenomena such as combustion in an internal combustion engine. There has been tremendous progress in lubricant technology over many years. Nonetheless, lubricants still ultimately break down in use to a point where their properties are insufficient for the particular intended use, and bulk replacement of the lubricant within its containment boundary is required, such as e.g., an "oil change" in a vehicle.

[0008] Under most circumstances, the optimum point at which a bulk lubricant change should occur is uncertain, from a performance standpoint and ultimately an economic standpoint. For example, while it is possible to make sophisticated rheological and compositional measurements of motor oil to indicate when such oil is failing to lubricate sufficiently, such measurements are not economically feasible to incorporate on vehicles sold to and used by customers. Such is also the case across a wide range of lubricant applications. Moreover, were such data available at a reasonable cost, the technical knowledge and experience required to interpret such data would generally preclude its use.

[0009] Thus the user of a lubricant, such as motor oil, is typically left with a simple prescription for lubricant change, such as "every 6000 miles or 6 months." Such a prescription results in some instances of taking a functioning lubricant out of service prematurely, thereby losing the economic value of the remaining life of the lubricant, and also creating a hazardous waste that must be dealt with before otherwise necessary. Such a prescription also results in some circumstances of taking a failing lubricant out of service too late, resulting in failure of the apparatus it was intended to protect. These latter circumstances also have obvious economic and waste generation implications, i.e., for example, a vehicle engine or parts rendered as scrap metal, and the cost of replacement thereof.

[0010] Heretofore, a number of patents and publications have disclosed particulate additives, to enhance the performance of lubricants, and many of such additive products are sold commercially. A lubricant additive containing ultrafine particles of polytetrafluoroethylene particles in a colloidal suspension is sold commercially as Slick 50® (by the SOPUS Products Corporation of Houston, Tex).


[0012] These fluoropolymer and metal alloy containing additives are meant to improve the lubricating properties of the lubricant to which they are added, rather than provide an indication when such lubricant is undergoing a loss of such lubricating properties. To the best of the applicants' knowledge, there has not been provided a lubricant composition, or a lubricant additive, which provides an easily understood indication of the lubricating properties of the lubricant, such as a visual indication that accurately indicates the point at which the lubricant should be replaced.
It is therefore an object of this invention to provide a lubricant additive, which provides an easily understood indication of the lubricating properties of a lubricant.

It is an object of this invention to provide a lubricant additive, which provides an easily perceived indication of the lubricating properties of a lubricant.

It is therefore an object of this invention to provide a lubricant additive, which provides an indication of the lubricating properties of a lubricant that can be visually perceived by the human eye.

It is therefore an object of this invention to provide a lubricant additive, which provides a spectral indication of the lubricating properties of a lubricant.

It is therefore an object of this invention to provide a lubricant additive, which provides a reflective indication of the lubricating properties of a lubricant.

It is therefore an object of this invention to provide a lubricant additive, which provides an indication of the lubricating properties of a lubricant that can be perceived in common ambient lighting conditions.

It is therefore an object of this invention to provide a lubricant additive, which is easily added and distributed throughout a bulk lubricant.

It is therefore an object of this invention to provide a lubricant composition comprising a lubricant condition-indicating additive distributed throughout a bulk lubricant.

It is therefore an object of this invention to provide a method for preparing a lubricant composition comprising a lubricant condition-indicating additive distributed throughout a bulk lubricant.

It is therefore an object of this invention to provide a method for distributing particles in fluids in response to local environmental stresses.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a lubricant additive comprising an indicating lubricant additive comprising a color-changeable polymer having an outer layer of a first color, and an intermediate layer of a second color.

In accordance with the present invention, there is further provided a lubricant sensing dipstick comprising a circuit housing, an elongated body having a proximal end and a distal end, and lubricant sensing means disposed at said distal end.

One aspect of the invention is based on providing an additive, which changes in appearance when subjected to shear and/or other adverse conditions present in the lubricant application. Such change in appearance dominates the overall appearance of the additive/lubricant mixture, thereby changing the perception of the appearance of the lubricant. It is not the intent of the present invention to entirely reformulate lubricants and impart them with condition-indicative properties, but rather to provide an additive composition which changes in appearance concurrently with loss of lubricant properties. In one embodiment, such change in appearance is relatively abrupt, occurring at the time or slightly in advance of the point in time at which the lubricant loses its lubricating properties to a degree where it is no longer suitable for its intended lubricating purpose.

This technique is advantageous because it is inexpensive compared to other approaches, and it can be adapted to any of a number of lubricant compositions. As a result of the invention, the user of a lubricant is able to easily determine the optimum time to replace such lubricant without complicated and expensive measurements and/or complex analyses.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described by reference to the following drawings, in which like numerals refer to like elements, and in which:

FIG. 1A is a perspective cutaway view depicting the general structure of a dendritic polymer;

FIG. 1B is a cross-sectional view depicting the general structure of a dendritic polymer.

FIG. 2 is a schematic representation of one indicating lubricant additive of the present invention comprising a dendritic polymer having an opaque outer layer and an intermediate layer containing dye functional molecules;

FIG. 3 is a schematic representation of another indicating lubricant additive of the present invention comprising a dendritic polymer having one or more intermediate layers comprising a first dye, and one or more outer polymeric layers comprising a second dye;

FIG. 4 is a schematic representation of one indicating lubricant additive of the present invention comprising a dendritic polymer having a three-layered indicating structure;

FIG. 5 is a schematic representation of a nano- or microcapsule that, when ruptured, provides color changing and indicating capabilities to the lubricant additive of the present invention;

FIG. 6A is a schematic representation of the presence of indicating capsules in a lubricant gap greater than the minimum allowable lubricant gap;

FIG. 6B is a schematic representation of the rupturing of indicating capsules by the shearing and/or crushing thereof in a lubricant gap that is less than the minimum allowable lubricant gap;

FIG. 7A is a schematic representation of the presence of dendritic polymers in a lubricant gap greater than the minimum allowable lubricant gap;

FIG. 7B is a schematic representation of the removal of an outer layer of a dendritic polymer capsules by the shearing and/or crushing action thereof in a lubricant gap that is less than the minimum allowable lubricant gap;

FIG. 8 is a schematic representation of a cross-sectional view of an internal combustion engine having a sensing dipstick for detecting the color change of a lubricant oil during use thereof;

FIG. 9 is a cross-sectional view of a general embodiment of the sensing dipstick of FIG. 8, comprising sensor means for sensing at least one property of the lubricant oil with which it is in contact;
FIG. 10 is a cross-sectional view of an embodiment of the sensing dipstick of FIG. 9, wherein the lubricant property sensor means thereof senses the color of such lubricant oil; and

FIG. 11 is a cross-sectional view of an embodiment of the sensing dipstick of FIG. 9, wherein the lubricant property sensor means thereof senses conductivity and/or pH and/or rheological properties of such lubricant oil.

The present invention will be described in connection with a preferred embodiment; however, it will be understood that there is no intent to limit the invention to the embodiment described. On the contrary, the intent is to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For a general understanding of the present invention, reference is made to the drawings. In the drawings, like reference numerals have been used throughout to designate identical elements. In describing the present invention, a variety of terms are used in the description. Standard terminology is widely used in the fields of color science and lubricant science.

For example, with regard to color science, one may refer to, U.S. Pat. No. 5,885,619 of Prater, “Method and apparatus for manipulating values in a color graphics system;” and U.S. Pat. No. 4,623,973 of Hoffrichter et al., the disclosures of which are incorporated herein by reference. These patents provide a detailed summary of the red-blue-green (RGB) additive color model, and the hue-saturation-luminance (HSL) and hue-saturation-value (HSV) subtractive color models, and the relationships therebetween.

In this disclosure, terminology with respect to color science and color pertaining to the use of the indicating lubricant additives of the present invention shall be recited in the context of the HSL color model, HSL referring to hue, saturation and luminance, respectively.

As used herein, the term “hue” is meant to indicate what is commonly called “color”, i.e., a location in the visible spectrum from violet to red.

As used herein, the term “saturation” is meant to indicate how pure or intense a color is. A fully saturated color is brilliant, while a minimally saturated color is dull and appears greyish.

As used herein, the term “luminance” is meant to indicate the perceived brightness of a color. A luminance of 0.0 is perceived as black to the human eye, and a luminance of 1.0 is perceived as white.

Further details regarding the mathematical relationships between the RGB, HSV, and HSL color models, and the relationships to the visual color perception of humans may be found in the cited patents of Prater and Hoffrichter et al.


A number of factors are considered in providing the indicating lubricant additives of the present invention. One factor is that the additives are to indicate the lubricant condition in a relatively straightforward way that does not require the use of sophisticated sensing and measurement instruments. The lubricant additives of the present invention are intended to be readable by a human with average visual color perception, and interpretable by a human of average intelligence, who does not have extensive technical training (e.g., a retail consumer, or an attendant at a typical franchised “quick change” automotive lube shop). The lubricant additives are further intended to be readable, most preferably, in commonly available ambient light such as outdoor daylight or internal dwelling or shop lighting, or in the presence of ultraviolet (UV) light provided by a low-cost, low wattage UV lamp.

The lubricant appearance resulting from the presence of the additive(s) of the present invention distributed therein is intended to be “readable” when it is present upon commonly available surfaces and objects, including but not limited to an automotive engine dipstick, or an inexpensive paper or cloth shop towel or rag. In preferred embodiments, the color of the commonly available surface or object is chosen in order to enhance the contrast thereof with the lubricant/additive mixture thereupon, in order to judge the lubricant condition. For example, the dipstick or towel may preferably be white if the appearance of the lubricant/additive mixture thereupon is generally quite dark.

In general, the lubricant additives of the present invention undergo an appearance change when subjected to the shear and other adverse conditions to which the lubricant itself is subjected, and such additives dominate the appearance of the lubricant/additive mixture, such that an overall change in “color,” i.e. a change in hue, saturation, and/or luminance of the mixture is perceived by a human. Such a perceived change in color can be the result of a change in properties including, but not limited to reflectance of certain wavelengths of light, absorption of certain wavelengths of light, refraction of certain wavelengths of light, and/or diffraction of certain wavelengths of light, scattering of certain wavelengths of light, emanations of certain wavelengths of light (e.g., fluorescence), and combinations thereof.

From a mechanistic standpoint, the changes in appearance of the lubricant/additive mixture when subjected to the shear and other adverse conditions to which the lubricant is subjected are achieved by phenomena including, but not limited to, the following: a change in molecular shape of at least one of the substances in the indicating additive; a rupturing of multiphase materials in the indicating additive, wherein such materials comprise a liquid phase material encapsulated within a solid phase material, and wherein the liquid phase material is of a different color than the solid phase material and the lubricant in which it is distributed; a rupturing of multiphase materials in the indicating additive, wherein such materials comprise a liquid phase material encapsulated within a solid phase material,
and wherein the liquid phase material undergoes a chemical reaction with other species present in the lubricant or the environment to produce a material that is of a different color than the solid phase material and the lubricant in which it is distributed.

[0055] In one embodiment of the present invention, there is provided an indicant lubricant additive that changes in appearance when the lubricant/additive mixture is subjected to the high shear and/or prolonged adverse conditions (e.g., high temperature) during use thereof. Such an indicating property occurs as a result of a change in molecular shape of one of the substances in such additive, or the loss of one of the substances in such additive. In this embodiment, the lubricant additive comprises a shape changing support molecule, which at the time of mixing into the lubricant (i.e., "time zero"), and at time of initial use, shows a first color dye. In one embodiment, as the lubricant ages due to high shear and/or prolonged adverse conditions, a second color dye is exposed, thereby altering the color of the lubricant/additive mixture.

[0056] In one preferred embodiment of the present invention, the shape changing molecule is a dendritic polymer, also referred to as a dendrimer. Such a dendritic polymer comprises a series of branched monomers that can be systematically layered. Much as a conventional polymer is a two dimensional chain of monomers, a dendritic polymer is a three dimensional sequentially formed structure of branched monomers that are successively added by controlled iterative chemical syntheses. Most commonly, dendritic polymers, or dendrimers, are formed with substantially spherical shapes; however, generally any three dimensional shape can be attained by using asymmetric monomers, or by changing the monomer shape during successive generations of synthetic additions to the structure.

[0057] At each successive layer addition, there is an opportunity to add functional molecules to the preceding outer layer of monomers. Accordingly, as each new generation of monomers is added to the dendrite, the functional molecules previously added are buried or enclosed within the inner cores of the growing dendrite. Examples of such dendritic polymers, the inner or initiator cores thereof, and relevant synthetic and purification methods therefor are disclosed in U.S. Pat. No. 6,703,504 of Selmon et al., "Conformationally constrained compounds as dendrimer cores;" U.S. Pat. No. 6,706,839 of Wilecox et al., "Chemical partitioning agents and methods of using same;" and U.S. Pat. No. 6,646,089 of Dvorin et al., "Hyperbranched polymers with latent functionality and methods of making same;" the disclosures of which are incorporated herein by reference. One may also refer to "Dendrimers and Other Dendritic Polymers," J. Freechett and D. Tomalia, eds., Wiley Interscience, 2002; and "Dendrimers—An Enabling Synthetic Science to Controlled Organic Nanostructures," D. Tomalia, R. Esfand, K. Mardel, S. E. Henderson, G. Holan, Chapter 20, Handbook of Nanoscience, Engineering and Technology (W. A. Goddard III, D. W. Brenner, S. E. Lyshevski, G. J. Infrate, eds.) CRC Press, Boca Raton, 20.1-20.34, (2002).

[0058] Numerous methods for synthesizing dendrimers are well known to those skilled in the art. Reference may be had to a review article written by Scott M. Grayson and Jean M. J. Frechet that appears in Chemical Reviews, volume 101, pages 3819-3867, 2001 entitled “Convert Dendrons and Dendrimers: from Synthesis to Applications.” This article discloses two general strategies for synthesizing dendrimers: the divergent approach and the convergent approach.

[0059] In general, the “divergent approach” begins the dendrimer synthesis at the core and adds one or more layers in succession around this core. Each additional layer corresponds to another “generation” of the dendrimer. Generally, there are three dendritic arrangements: layered, segmented, and tailored. In a “layered” arrangement, the first generation and second generation are constructed from the same monomer. In a “segmented” arrangement, consecutive generations are made from different monomers. This is sometimes referred to as a “layered copolymer.” Grayson’s review article describes layered copolymers as containing “...two or more types of repeat units that are segregated in a layerwise fashion in the final dendritic product” (see page 3856 of aforementioned Grayson article). A “tailored” arrangement is one in which one “branch” of the dendrimer has been customized such that it is different than the other branches in the same generation. Reference may be had to page 3855 of the aforementioned Grayson article.

[0060] In contrast to the divergent approach, the “convergent approach” begins the synthesis of the dendrimer at the outermost generation and works inward, eventually leading to the coupling of the two halves of the dendrimer, thus producing the core as the final synthetic step. The convergent approach is particularly convenient due to its modularity. As stated by Grayson, “The convergent approach has seen extensive use in the construction of functional macro-molecules because of its ability to modify dendrons at both the focal point and the chain ends. This modularity is especially helpful in design optimization because the same dendritic structure can be modified, after the dendron synthesis, to vary the number and chemistry of functional moieties in the resultant dendrimer.” By selecting alternating monomeric units, a dendritic “copolymer” can be made. As is known to those skilled in the art, and as discussed above, these copolymers can be “layered”, “segmented”, or “tailed”.

[0061] It is clear from the Grayson review article that numerous dendrimers have been made by linking aromatic alcohols in a dendritic fashion. One such synthesis is summarized in Structure IA. It is noteworthy that many organic dyes also contain an aromatic alcohol that makes them particularly well suited to incorporation in a dendrimer. Structures 2A-21 provide illustrations of a subset of some of the common organic dyes. In one embodiment of the present invention, an organic dye with at least two aromatic alcohols is used. In one such embodiment, a Tropaeolin O derivative is used.
Structures 1A AND 1B: Dendrimer Synthesis

\[
\text{STRUCTURE 1A: KNOWN}
\]

\[
\text{dendrimer}
\]
Conventional synthetic chemistry has been adapted to incorporate functional repeating units in a dendritic structure. As discussed on page 3854 of the Grayson review article, "The convergent approach also permits the incorporation of functional repeat units. Because the repeat units comprise the majority of the dendritic structure, they represent an ideal location for multiple functional moieties. In addition to the numerous examples of conjugated dendrimers previously discussed, the convergent approach has been demonstrated as a viable route toward the preparation of dendrimers with a range of repeat units including: fullerene, quaternary ammonium salt, pyridine, TTF, triarylamine, carbazole, azobenzene, liquid crystalline, and chiral repeat units."

One may use conventional synthetic chemistry to attach organic dyes at specified generational levels of a dendrimer. For example, one may incorporate a dye in generation 1 of a dendrimer as seen in Structure 1B. In Structure 1B, the first generation (R=azo dye) is bound to the core. In the embodiment depicted in Structure 1B, the second generation (R=H) does not contain a dye. In another embodiment (not shown), the second generation contains a dye which is substantially the same as the dye found in the first generation. In yet another embodiment (not shown) the second generation contains a dye that is substantially different (R group is altered) from the dye in the first generation. In other embodiments, no dye is incorporated in the first generation, but at least one dye molecule is covalently incorporated in a second or subsequent generation.

One need not utilize dendrimers based on aromatic alcohols. Poly(propyleneamine) dendrimers are also well suited for use with the present invention. One may incorporate dyes through the aromatic sulfite groups common to organic dyes. Reference may be had to a paper by Holger Stephan et al. appearing in Organic Letters, volume 2, pages 2343-2346, 2000, entitled "pH-Controlled Inclusion and Release of Oxyanions by Dendrimers Bearing Methyl Orange Moieties."
One skilled in the dendrimer art is aware of many methodologies to functionalize dendrimers at multiple generation levels. Dendrimers have been previously customized to support specific molecules on the surfaces (highest generation) of the dendrimer. For example, in a review article by Heerbeek et al. (Chem. Rev. volume 102, pages 3717-3756, 2002) entitled “Dendrimers as supports for Recoverable Catalysts and Reagents” the use of dendrimers as catalyst supports is discussed. One such dendrimer incorporates a visible dye to the surface of the dendrimer. Albrecht et al. synthesized a series of polybenzyl ether dendrimers containing a pinocarboxylic acid (Ni, Pt) at the focal point of the wedge. Coordination of SO₃⁻ to the pinocarboxylic acid complex resulted in a change in color of the dendrimer solutions from colorless to orange. The obtained SO₃⁻ complexes were utilized as dyes to study the recoverability of these dendrimers by membrane filtration. The generation dependent leaching of the dendrimers from a membrane-capped immersion vial was followed over time by UV-Vis spectroscopy. The higher the generation number (i.e. larger the dendrimer) the slower the diffusion of the dendrimer. The organic dye, Methylene Blue, was incorporated into the highest generation of a dendrimer as disclosed in a paper by Holger Stephan et al. appearing in Organic Letters, volume 2, pages 2343-2346, 2000, entitled “PDI-Controlled Inclusion and Release of Oxyanions by Dendrimers Bearing Methyl Orange Moieties.”

Dyes have similarly been incorporated into the core (generation zero) of dendrimers. In a review article by Heerbeek et al. (Chem. Rev. volume 102, pages 3717-3756, 2002) entitled “a dye Red-1-core-functionalized dendrimer containing a thioe-protected periphery was prepared. The HMOP-linker was introduced on the dendrimer periphery by deprotecting the peripheral amines, condensation of an activated ester of acetylated hydroxymethylphenoxyacetic acid and de-esterification.”

In a paper entitled “Characterization of Cyanine Dye-Labeled Poly(N-isopropylacrylamide) Core/Shell Micogels Using Fluorescence Resonance Energy Transfer” Jordan et al. discloses methods for covalently incorporating dyes into polymeric materials. Additional synthetic approaches have been developed to covalently incorporate various dyes at the core of dendrimers. Reference may be had to The Journal of the American Chemical Society, volume 122, pages 12385-12386, 2000, in a paper by Freeman et al. entitled “Dendrimer-Containing Light-Emitting Diodes: Toward Site-Isolation of Chromophores”. Some of the “dyes” are active in non-visible regions of the spectrum. Reference may be had to Chem. Rev. volume 101, pages 3819-3867, 2001, by Grayson et al. “Dendrimers have also been attached to fluorescent cores in order to modify the properties of the dye. The attachment of dendrons to oligothiophenes improved the solubility of the oligothiophenes in organic solvents, whereas the placement of appropriate dendritic substituents on porphyrins chromophores yielded water [soluble] dyes.”

The use of dendrimers as “nanocounters” to non-covalently encapsulate dyes is discussed in a paper entitled “Dendrimers with Both Polar and Aporal Nanocontainers Characteristic” by Yukutoku et al. published in the Journal of the American Chemical Society, volume 126, pages 15636-15637, 2004. The amount of dye incorporation was found to be related to the dendrimer generation, with higher generations able to incorporate more dye molecules. The incorporation of other host molecules (including the organic dye Acid Red) into dendrimers has also been discussed by Ghosh in an article appearing in Macromolecules, volume 36, pages 9162-9169, 2003, entitled “Nanoscale Solution Structure and Transfer Capacity of Amphiphilic Poly-amidoamine” Dendrimers Having Water and Polar Guest Molecules Inside.” The Grayson review Article (Chem. Rev. volume 101, pages 3819-3867) also briefly discusses the use of dendritic nanocontainers. “For example, Meijer et al. have described an elegant ‘dendritic box’ that can encapsulate various small organic molecules and control their release by modifying the steric crowding of the dendritic periphery. Synthetic approaches have been developed that allow the functionalization of both the interior and exterior of these versatile macromolecules.” In one embodiment of the present invention a dye molecule is encapsulated within a dendritic box and is only released upon degradation of the box. When the dye is liberated, the dye molecules is quickly solvated. The solvated dye molecule is no longer encapsulated, its spectrum is altered in response to its new environment. Thus, there now exists a convenient way to monitor degradation of the dendritic box as well as monitor the wear on the box.

The electrostatic bonding of organic dyes to dendrimers has been discussed in a paper by Karakitsos et al. in Langmuir, volume 18, pages 10363-10371, 2002, entitled “Spectroscopic Characterization of Azo Dye Aggregation on Dendrimer Surfaces.” This article discusses the use of organic dyes such as Naphtho orange, Acid Red, Chrome Violet, Ethyl Orange, Methylene Orange, and Erichrome Blue Black in conjunction with dendrimers. This article provides an excellent explanation of the correlation between dendrimer generation and color of the dyes aggregated with the dendrimer.

As stated on page 10364 of this paper “...the optical properties of dye aggregates vary with the relative orientation of the monomers and the size and structure of the molecular aggregate...we use the surface of polymeric dendrimers as a platform on which to anchor ionic dyes.” As the dendrimer generation increased, the number of exposed surface functional groups increases. These exposed surface groups alter the color of the dye. Thus, the dye color may be correlated to the dendrimer generation.

In one embodiment of the instant invention, a generation N dendrimer is degraded to a generation N-1 dendrimer. This degradation results in a shift in the color of the associated dye.

It is to be understood that in the following description, dendritic polymers having a generally spherical shape are described and illustrated in the associated Figures, but that dendrimers having other shapes such as e.g., approximately a box shape are considered to be within the scope of the present invention. It is also to be understood that although certain dyes are cited as examples of dyes that may be incorporated into the additives of the present invention, many other dyes such as those depicted herein in Structures 2A-21 may also be used.

FIGS. 1A and 1B are schematic representations of a the general structure of a dendritic polymer used in the indicating lubricant additives of the present invention. FIG. 1A is a perspective cutaway view of a dendritic polymer, and
FG. 1B is a cross-sectional view of a dendritic polymer. Referring to FIGS. 1A and 1B, dendritic polymer 1 comprises an inner initiator core 5, a first layer or generation 10 comprised of functional molecules 11, a second layer or generation 20 comprised of functional molecules 21, a third layer or generation 30 comprised of functional molecules 31, and a fourth layer or generation 40 comprised of functional molecules 41. For the sake of simplicity of illustration, in FIG. 1A, functional molecules 11, 21, 31, and 41 are represented as simple spheres; and in FIG. 1B, functional molecules 11, 21, 31, 41, and 51 are represented as simple junctures of branches of the dendrimer 1. Generations 10, 20, 30, and 40 of FIG. 1A comprise an interior area containing branch upon branch of repeat units having radial connectivity to core 5.

In synthesis of dendrimer 1, each of the generations or layers is synthesized in succession. At the starting point, “generation zero,” or Gen, there is present only core 5 with branches 8 terminating at terminal moieties 9. Subsequently, layer 10 is synthesized or grown, comprising functional molecules 11 having branches 18 terminating at terminal groups 19, layer 20 is added, comprising functional molecules 21 with terminal groups or termini 29; layer 30 is added, comprising functional molecules 31 with terminal moieties 39; and layer 40 is added, comprising functional molecules 41 with terminal moieties 49. Further synthesis of dendrimer 1 may continue with a fifth layer (L=5), comprising functional groups 51, and so forth, on through an Nth layer, having functional molecules with terminal moieties 99.

Although in FIG. 1B, there is illustrated a core 5 having three branches, many other cores having other initial branched configurations may be used, such as e.g., ethylenediamine, cystamine, 1,6-diaminohexane, 1,4-diaminobutane, or 1,12-diaminododecane. Terminal moieties known in the art may be e.g. amidoethanol, amidoethylhexanolamine, carbethoxypropyldimethoxymethyl, hexylamine, polyethyleenglycol, sodium carboxylate, succinimide acid, and tris(hydroxymethyl)aminomethane.

In the preferred embodiment, this layered polymeric architecture is utilized, wherein one or more of the intermediate layers, e.g., layer 30, in the dendritic polymer comprises at least a first dye as a functional molecule disposed in such layer or layers. One or more outer polymeric layers, e.g., layer 40, are provided that overlay this layer or layers comprising such first dye.

FIG. 2 is a schematic representation of one indicating lubricant additive of the present invention comprising a dendritic polymer having an opaque outer layer and an intermediate layer containing dye functional molecules. Referring to FIG. 2, overlaying layer or layers 140 provide opacity, wherein external light 999 of some wavelength or wavelengths either does not penetrate inwardly through the functional molecules 141 in outer 23 layer 140 to reach the dye molecules 131 in layer 130, or reflected and/or emitted light 998 from dye molecules 131 does not penetrate outwardly through the outer layer where such light becomes visually or instrumentally detectable. Accordingly, the color of the dye of the intermediate layer(s) 130 is rendered not visible to the eye and/or not detectable by a calorimetric instrument. In a variant of this embodiment, the color appearance of the intermediate layer(s) 130 is rendered significantly muted so as to have a much less saturated appearance as a result of the presence of the opaque overlaying layer 140.

In either circumstance, when the lubricant additive containing dendritic polymer 100 is exposed to the adverse conditions in the lubricating or cutting application, outer layer 140 with opaque molecules 141 having terminal groups 149 are removed from dendritic polymer 100, thereby exposing intermediate layer 130 containing dye molecules 131, which emanate light 998 to the eye of the observer (not shown), or to a calorimetric instrument (not shown). Such opaque molecules are removed either by the extreme mechanical action in the application, which breaks the bonds with layer 130, or by the thermal degradation of such bonds, or by chemical reaction with various contaminant such as e.g., gasoline, water, dirt, ions, and other species that destroy such outer bonds.

In another variant of this embodiment, the dye molecules 131 in layer 130 react with a metal, peroxide, water, or ion, resulting in a change in the color of the dye 131, and consequently, a change in the color emanating from layer 130 of dendritic polymer 100. In yet another embodiment, dye molecules 131 are fluorescent dye molecules, and external light 999 is ultraviolet light. When layer 140 is sufficiently removed from dendritic polymer 100, and fluorescent dye molecules 131 are exposed to and stimulated by ultraviolet light 199, such molecules emit light 998, which is then detected by the eye of the observer, or a calorimetric instrument.

In all embodiments, there is a significant difference in color, either visually or instrumentally (i.e. measured by a calorimetric instrument), between the dendritic polymer 100 having at least a first dye disposed in an intermediate layer 130 thereof and enclosed within an opaque layer 140, and such polymer 100 wherein such opaque outer layer 140 is removed, thereby exposing dye containing intermediate layer 130. Accordingly, when the outer layer 240 comprising second dye 241 is present on the dendritic polymer 200, and polymer 200 is illuminated with light 997, the appearance of the dendritic polymer 200 is the color of reflected or emitted light 996 emanating from such second dye 241. Substantially none of light 997 penetrates to layer 230 of polymer 200.

When outer layer 240 containing second dye 241 is removed by dissolving, chemically reacting or etching,
thinning, wearing, abrading, fracturing and shedding, or otherwise subtracting such layer 240, ambient light 997 reaches first dye 231 in intermediate layer 230. The appearance of the dendritic polymer 200 under these circumstances is the color of reflected or emitted light 995 emanating from such second dye 241.

[0083] In this embodiment, there is a significant difference in color, either visually or instrumentally, between the dendritic polymer 200 having the first dye 231 as the functional molecule disposed in its outer layer 230 (when layer 240 has been removed), and such polymer 200 having the second dye 241 disposed in its outer layer 240. Accordingly, by dissolving, chemically reacting or etching, thinning, fracturing and shedding, or otherwise subtracting such an outer layer 240 comprising the second dye 241, a color change is effected in the dendritic polymer material 200, from an appearance mainly defined by the hue of the second dye 241, to an appearance mainly defined by the hue of the first dye 231.

[0084] Thus, for any of these preferred embodiments, when the indicating lubricant additive is provided with a dendritic polymer comprising an outer opaque layer over an intermediate layer comprising a first dye, or an outer layer comprising a second dye over an intermediate layer comprising a first dye, when such outer layer is removed, thinned, or otherwise subtracted from such intermediate layer, a visually and/or instrumentally detectable color change results in the dendritic polymer, in the lubricant additive, and in the lubricant through which the lubricant additive is distributed.

[0085] One preferred class of lubricant additives of the present invention comprise such dendritic polymers wherein the outer layers thereof are dissolved, chemically reacted or etched, thinned, or otherwise subtracted in general from the underlying intermediate layers as a result of the high shear and/or other adverse conditions present in the lubricating application. Such subtraction of the outer layer or layers occurs in a predictable manner that correlates with the occurrence of the lubricant losing its lubricating properties and being rendered unsuitable.

[0086] Thus in the instance of blending a lubricant additive into a lubricant wherein the additive comprises a dendritic polymer having an opaque outer layer and an intermediate layer comprising a first dye, at time zero the lubricant additive has an insignificant effect on the appearance of the lubricant. At such time as when the lubricant loses its lubricating properties and the outer opaque layer is subtracted from the dendritic polymer in the additive, the color of the first dye in the intermediate layer is exposed and dominates the color of the lubricant/additive blend, thereby changing the appearance thereof and indicating the loss of lubricating performance.

[0087] In the instance of blending a lubricant additive into a lubricant wherein the additive comprises a dendritic polymer having a second dye disposed in an outer layer and a first dye disposed in an intermediate layer, at time zero the lubricant additive renders the appearance of the lubricant as being of the color of the second dye. At such time as when the lubricant loses its lubricating properties and the outer layer comprising the second dye is subtracted from the dendritic polymer in the additive, the color of the first dye in the intermediate layer is exposed and dominates the color of the lubricant/additive blend, thereby changing the appearance thereof and indicating the loss of lubricating performance.

[0088] In a further embodiment (not shown), wherein the lubricant comprises nanoparticles such as is disclosed in U.S. Pat. No. 5,523,006 of Strumban, the outer layer 240 comprising the second dye 241 of the dendritic polymer 200 dominates the color of the lubricant, supressing or eliminating the undesirable muddy appearance that would otherwise be present in such nanoparticle lubricants.

[0089] In a further embodiment, there is provided a lubricant additive comprising a dendritic polymer having a multi-layered indicating structure comprising at least three functional layers. FIG. 4 is a schematic representation of such an indicating lubricant additive of the present invention, comprising a dendritic polymer having an three-layered indicating structure. Referring to FIG. 4, and in one preferred embodiment, the indicating lubricant additive comprises a dendritic polymer 300 comprising a first intermediate layer 320 comprised of a first dye 321, a second intermediate layer 330 comprised of a second dye 331, and an outer opaque layer 340. Such an additive provides the capability to indicate an “alert” condition with a first color change that occurs when opaque layer 340 is removed and layer 330 containing dye 331 is exposed, and a “fail” condition with a second color change that occurs when layer 330 is removed and layer 320 containing dye 321 is exposed. In another embodiment with similar capability, there is provided a lubricant additive comprising a dendritic polymer 300 comprising a first intermediate layer 320 comprised of a first dye 321, a second intermediate layer 330 comprised of a second dye 331 and an outer layer 340 comprised of a third dye 341.

[0089] The physical properties of such dendritic polymers and the thermal stability, chemical reactivity, solubility, shape, elasticity, and shear sensitivity thereof are tunable depending on the specific type of monomer used, the number of iterative generations (layers) grown, and additional treatments or functional chemical groups included. Thus, when such dendritic polymers are provided in a lubricant additive that is blended with a lubricant/oil or cutting fluid, the exposure of such dendritic polymer to the high shear, pressure, attrition, combustion products, and other adverse effects (in e.g., an internal combustion engine, or a cutting application) results in such dendrimer undergoing a shape change entailing a dissolving, chemically reacting or etching, thinning, fracturing and shedding, or otherwise subtracting of the outer layer thereof, thereby revealing the underlying dye or dyes in the inner core thereof, and thereby effectively changing the color of the lubricant.

[0091] One preferred dendritic polymer that may provide such color changing and indicating capabilities is a Poly(allylamine) (PAMAM) dendrimer comprising a core of ethylenediamine, at least one intermediate shell layer of PAMAM dendrimer, carboxymethyl ester-terminated [i.e., EDA]-dendri-PAMAM-(CO2Me)x2, in which is disposed a yellow dicyanovinylaline dye as disclosed subsequently in this specification, and an outer surface layer of hexylamide. In a preferred embodiment, such dendrimer comprises between about six and about sixteen generations, with the dye being disposed in the outermost intermediate layer as described previously in this specification. It is preferable also that the outer surface layer be hydrophobic.
The rate of degradation and subtraction of the outer layer is controllable to a substantial extent through the choice of total dendrimer diameter, or number of generations. For example, if there is provided an indicating dendritic polymer of about generation 16, the colored intermediate layer thereof stays hidden longer than if the dendritic polymer is about generation 6, because it will take longer to break down a generation 16 dendrimer than generation 6 when such polymer is exposed to adverse conditions such as, e.g., shear, heat, and/or oxidation/reduction reactions. Accordingly, the diameter distribution of the lubricant additive is to be matched to the specific stabilities of the lubricant used and the adverse conditions that are present in the lubricating application.

In one preferred embodiment, this dendritic polymer is formulated as a lubricant additive further comprising additional additives such as friction reducing additives, anti-oxidant agents that prevent oxidation of constituents in the lubricant, or reducing agents that reduce oxidized materials that accumulate in the oil into neutral particles, rendering such materials less harmful to the engine and further extending the life of the oil. Examples of such additives may be found, e.g., in U. S. Pat. No. 6,764,984 of Beatty, “Fluorinated lubricant additives,” U. S. Pat. No. 6,689,725 of Gao, “Lubricant composition for diesel engines,” U. S. Pat. No. 6,759,375 of Curtis et al., “Use of an amide to reduce lubricant temperature,” U. S. Pat. No. 6,638,897 of Ogino et al., “Lubricant oil composition for internal combustion engines (lub859),” and in U. S. Pat. No. 6,582,485 of Julius et al., “Fuel and lubricant additives,” the disclosures of which are incorporated herein by reference.

The lubricant additive is preferably made by suspending the dendritic polymer in a fluid carrier or vehicle using relatively low shear mixing and blending processes, including dissolution techniques, emulsion techniques, and direct in-situ synthesis of the successive generations of the dendrimer in the fluid carrier medium. Such fluid carrier is preferably a hydrocarbon fluid carrier for compatibility with hydrocarbon lubricants, although also a water-based fluid carrier may be used for compatibility with aqueous lubricants or cutting fluids.

In a lubricating application, the adverse conditions that result in the subtraction of the outer layer of this dendritic polymer, and cause the resultant change in color in the lubricant additive in which it is distributed are high liquid shear, mechanical impact (i.e., solid surface-solid surface contact), temperature, pH, and the presence of oxidizing agents. The parametric values of these particular conditions that result in the desired color change/indication are tunable by the choice of initiating core, monomer, and the number of generations of growth in the dendrimer.

In other embodiments, other shape changing support molecules include proteins, polymers, ligands, gels, etc. Other functional molecules that may be included in the lubricant additive are pigments, lubricants, nanoparticle lubricants, environmentally friendly remediation agents, or active “reagents” to clean or refresh the lubricant oil. Other fluids that may be included in the lubricant additive are inks, sol-gel products (e.g., aerogels, zergols), gasses, water, and the like. Suspension of the dendrimer could include dissolution techniques, emulsion techniques, etc.

In another preferred embodiment of the present invention, there is provided an indicating lubricant additive comprising a nano- or microcapsules containing a dye. Such dye containing microcapsules are suspended in a fluid of another color that is preferably lighter than the color of the encapsulated dye. When a particular degree of stress occurs within the system being lubricated, such as thermal or shear stress to which oil in an internal combustion engine is subjected, the microcapsules are caused to burst or pinch thereby causing the dye molecules to spill out from within the ruptured capsules, thereby causing the lubricant color to change.

A nano- or micro-capsule is a substantially spherical shell of polymer or lipids created through self assembly of the lipids in the presence of a hydrophilic medium such as e.g., water. Alternatively, such nano/micro-capsules may be formed through the process of emulsion, much as oil and vinegar form a two-phase milieu of droplets of one phase in a continuum of the second phase, rather than mixing in a homogeneous single phase, in a manner similar to that in which a cellular membrane self assembles in an aqueous environment.

Specific nanocapsules are disclosed in recent patents. For example, one may refer to U. S. Pat. No. 6,713,533 of Panzer, “Nanocapsules and method of production thereof,” which discloses nanocapsules of between about 50 nanometers and 10 micrometers in diameter, having an outer layer of at least two different crosslinked polymers, and optionally carrying a biologically active compound therein. One may also refer to U. S. Pat. No. 6,685,468 of Edelman et al., “Organosilicon nanocapsules,” which discloses nanocapsules having a nanoscale core and an organosilicon shell. One may further refer to U. S. Pat. No. 6,667,043 of Podurbin et al., “Technical di- and triglyceride mixtures” which discloses technical di- and triglyceride mixtures which are obtained by partial transesterification of vegetable oils with methyl esters. The disclosures of these United States patents are incorporated herein by reference.

FIG. 5 is a schematic representation of one embodiment of a nano- or microcapsule that, when ruptured, provides color changing and indicating capabilities to the lubricant additive of the present invention. Referring to FIG. 5, nanocapsule 500 comprises a lipid microcapsule 501 that is stabilized in an hydrophobic liquid 70 (e.g., a hydrocarbon oil) by a surface treatment that provides an additional shell 502, wherein the inner surface 504 thereof comprising hydrophobic functional groups 506 contacts the lipid microcapsule 501, while the outer surface 508 of such shell comprises hydrophilic groups 510 that prevent the oil 70 from leaching and absorbing the internal contents 520 of the lipid capsule. Thus such a microcapsule 500 can be formed so that the contents 520 thereof may be almost any fluid, including dyes.

For example, in one embodiment, one could use a red dye filled microcapsule in a lubricant additive in a lubricant that is dyed yellow. The original color is e.g., a bright yellow with a hint of orange. As the oil is used in e.g., an IC engine, either heat or shear stress may cause a certain number of the microcapsules to break apart, releasing their dye particles. As the engine continues to run, a greater number of the microcapsules spill their dye particles into the oil, causing the color to become redder with use. This process may be further controlled by varying the number of shells around a microcapsule, thereby requiring more time to...
degrade and burst, and/or by chemically attaching yellow dye to the outside of the microcapsule or within the lipids or proteins of the microcapsule to achieve greater color change distinction.

[0102] In one embodiment, there is provided an organosilicon nanocapsule as disclosed in U.S. Pat. No. 6,689,468 of Edelmann et al. containing within the shell thereof one or more of the yellow dicyanovinylamine dyes as disclosed in U.S. Pat. No. 5,476,746 of Janssens et al., “Black colored dye mixture for use according to thermal dye sublimation transfer,” the disclosures of which are incorporated herein by reference. In a further embodiment, nanocapsule 500 comprises a phospho lipid layer wherein during use as an indicating lubricant additive, the highly polar nature of the membrane 502 thereof causes such membrane to adhere to metal surfaces in a protective layer, while the dye contents 520 thereof are discharged into the surrounding lubricant 70.

[0103] In other embodiments, other suitable nano/micro capsule shell materials may include fullerenes, polymers, ligands, interlocking nanoparticles or chemical groups, or rectangular cage materials. Such cage materials are preferably made prior to dye association and then impregnated with dye molecules via doping mechanisms or diffusion.

[0104] Examples of suitable nano/micro capsule shell materials may be found e.g., in U.S. Pat. No. 6,703,193 of Laney et al., “Microbead and immiscible polymer voided polyester for imaging media,” U.S. Pat. No. 6,692,769 of Ishibashi et al., “Sustained-release particles,” U.S. Pat. No. 6,613,721 of Kermizan et al., “Colloidal suspensions for use as a lubricant or additive,” and U.S. Pat. No. 5,932,539 of Stupp et al., “Biodegradable polymer matrix for tissue repair,” the disclosures of which are incorporated herein by reference.

[0105] Although the performance of lubricants may be specified by a range of rheological and other properties, one critical parameter that must be maintained in a lubricating application (as opposed to a cutting application) is a minimal film thickness of lubricant or a minimum lubricant gap between the lubricated surfaces that are in motion at different velocities. Such a minimal film thickness prevents surface-to-surface contact between the moving surfaces, and thus prevents sudden and extreme wear and heat buildup therebetween.

[0106] In some lubricant applications in an internal combustion engine, the lubricant is provided by a pressure feed of the lubricant into the lubricant gap, such as e.g., by an on-board oil pump that forces oil outwardly from internal passageways in the engine crankshaft, thereby lubricating the main and rod journals thereof. In other applications in an internal combustion engine such as e.g. camshaft lobe-valve lifters contact, or valve stem-rocker arm contact, the lubricant gap is maintained only by the wetting of the lubricated surfaces of the respective parts, and the viscous or viscoelastic resistance of the lubricant to displacement from such gap by shear and pressure forces that are present. In either circumstance, as the lubricant begins to fail (or in the former instance, as the oil pump begins to fail), the lubricant gap decreases, and conditions approach the highly undesirable onset of metal-to-metal contact and imminent part failure.

[0107] In one preferred embodiment of the present invention, a lubricant additive is provided comprising nano/microcapsules having a characteristic dimension (such as e.g., diameter if approximately spherical in shape) that is within a particular dimensional range, such that when the lubricant approaches failure and the lubricant gap between at least some of the lubricated surfaces in motion decreases below a particular acceptable minimum, such nano/microcapsules are ruptured.

[0108] It is known that the typical desired running clearances between lubricated surfaces in an internal combustion engine are between about 30 and about 130 microns. These desired clearances depend upon the pressure and volume capacity of the lubricant oil pump, the engine operating conditions, and the particular pair of surfaces being lubricated, such as e.g., rod bearing and crankshaft journal, main bearing and crankshaft journal, cam bearing and camshaft journal, or piston and cylinder wall clearance. See, for example, ASTM D6709-03a, “Standard Test Method for Evaluation of Automotive Engine Oils in the Sequence VIII Spark-Ignition Engine,” the disclosure of which is incorporated herein by reference.

[0109] In the instance where there is a stationary bearing such as a connecting rod or main bearing disposed around a crankshaft journal, such bearing clearance is the difference between the diameter of the journal and the inside diameter of the bearing. Thus the average gap between the bearing surface and the journal surface around the perimeters thereof is one-half of the bearing clearance, i.e. between about 15 and about 65 microns, assuming the journal and bearing are perfectly round and their central axes are co-linear. If the lubricant and the lubricating system is functioning ideally, this average gap is maintained as the lubricant gap.

[0110] In actuality, this lubricant gap will vary during the operation of the engine, because of variations in manufacturing tolerances of the parts, and non-uniform forces on the parts. (In particular, the reciprocating action and the combustion-driven piston forces on a connecting rod are non-uniform in time.) The lubricant gap will also decrease as the lubricating properties of the lubricant degrade during operation of the engine. Consequently, the lubricant will become very small in localized areas of the bearing, and eventually, bearing-to-journal (solid surface to solid surface) contact will occur, with attendant scuffing and/or welding of the solid parts.

[0111] Thus it will be apparent that it is desirable to maintain a minimum lubricant gap between such surfaces of at least about 20 percent of the minimum average gap between the bearing surface and the journal surface, i.e. a lubricant gap of about 6 microns. The maintenance of this lubricant gap, and the detection of conditions wherein it is being approached in the operation of the engine are important in ongoing operation of the engine without damage thereto.

[0112] In one embodiment, the nano/microcapsules of the lubricant additive are provided with a characteristic dimension of between about 1.5 and about 2.5 times the minimum desired lubricant gap, i.e. between about 9 microns and about 15 microns. Such microcapsules will rupture and provide an indication of approaching lubricant failure well in advance of such failure. In another embodiment, the nano/macrocapsules of the lubricant additive are provided with a characteristic dimension of between about 1.0 and about 1.5 times the minimum desired lubricant gap, i.e.
between about 6 microns and about 9 microns. Such microcapsules will rupture and provide an indication of approaching lubricant failure slightly in advance of such failure.

[0113] Fig. 6A is a schematic representation of the presence of indicating capsules in a lubricant gap greater than the minimum allowable lubricant gap, and Fig. 6B is a schematic representation of the rupturing of indicating capsules by the crushing thereof in a lubricant gap that is less than the minimum allowable lubricant gap. Referring to Fig. 6A, in the lubricating application, a first part 802 is in motion relative to a second part 804, as indicated by arrow 899. It is to be understood that for the sake of simplicity of illustration, Figs. 6A and 6B (and subsequent Figs. 7A and 7B) are not drawn to scale, and that the curvature of such surfaces is exaggerated compared to the gap between the parts therein. Such parts may be e.g. a crankshaft moving within a main journal bearing or a rod journal bearing; or a cam lobe moving against a cam follower; or a pair of gear teeth moving relative to each other. Referring again to Fig. 6A, parts 802 and 804 are separated by an acceptable lubricant gap 989, and nanocapsules 500 containing dye 520 are entrained within the high shear flow field of lubricant 70 therebetween, without rupture of such nanocapsules 500.

[0114] Referring now to Fig. 6B, as lubricant 70 undergoes degradation during use, and the lubricating properties thereof diminish, the lubricant gap between parts 802 and 804 decreases, to an unacceptable gap 988. Under this circumstance, nanocapsules 500 are compressed in gap 988, and the shearing and/or crushing action between parts 802 and 804 rupture capsules 500, resulting in spilled dye 521 mixed into lubricant 70, thereby indicating by a color change of lubricant 70 that such lubricant is failing. Such indication occurs before lubricant gap becomes zero, i.e. before contact of parts 802 and 804 occurs, thus providing a warning before catastrophic failure of such parts occurs.

[0115] In other embodiments, the nano/macrocapsules 500 of the lubricant additive are provided with a less structurally strong shell, which enables shear-driven rupture thereof. In this embodiment, the exposure of such capsules to the extremely high shear conditions that occur when the running clearances between moving parts approaches the minimum lubricant gap, and the resulting shear forces upon such capsules are sufficient to rupture the capsules and provide an indication of approaching lubricant failure. In such an embodiment, the nanocapsules are preferably between about 3 nanometers and about 500 nanometers in diameter, and more preferably between about 100 nanometers (0.1 micron) and about 500 nanometers (0.5 micron) in diameter.

[0116] It is not necessary that such capsules are of a characteristic dimension greater than or equal to the minimum lubricant gap. A typical shear rate in a minimum acceptable lubricant gap between engine parts is between about 10^4 and about 10^6 seconds^-1. Thus in another embodiment, the lubricant additive comprises nano/macrocapsules that rupture when exposed to shear greater than at least about 10^6 seconds^-1, and such microcapsules rupture when the minimum lubricant gap between parts is approached, and the resulting shear rate therebetween approaches or exceeds about 10^6 seconds^-1. In one preferred embodiment, such nano/macrocapsules have a characteristic dimension of between about 0.05 microns and about 0.5 microns. This preferred lubricant additive has the added advantage of being more compatible with internal combustion engines that use typical automotive oil filters. Such oil filters are designed to prevent the passage of substantially all particles greater than about 30 microns in diameter, and thus the nano/macrocapsules of the lubricant additive are not trapped or collected by such oil filters.

[0117] In a further embodiment, such nano/macrocapsules are formed from a polymeric material with a specific glass transition temperature that is matched to the desired operating temperature of the oil. It is known that the typical operating temperature of oil in an IC engine is between about 135 degrees Centigrade (°C.) and about 145° C. (See, for example, ASTM D6709-03a, “Standard Test Method for Evaluation of Automotive Engine Oils in the Sequence VIII Spark-Ignition Engine.”) The lubricating properties of such oil may degrade significantly if the engine overheats and the temperature of such oil exceed 150° C., which is the maximum temperature at which ASTM viscosity tests on lubricating oils are performed. (See, for example, ASTM D4624-93, “Standard Test Method for Measuring Apparent Viscosity by Capillary Viscometer at High-Temperature and High-Shear Rates,” the disclosure of which is incorporated herein by reference.

[0118] Accordingly, in one embodiment, the microcapsules are provided with an outer shell having a glass transition temperature of between about 145° C. and about 150° C. Thus when the oil reaches a temperature at which its properties begin to degrade significantly, the walls of the microcapsules are significantly softened (and possibly melted to form a liquid phase), such that they are subsequently ruptured by the normal shear and pressure forces that are present in the lubricant application. It will be apparent that in other applications wherein the lubricant operating temperature is different, or the resistance thereof to thermal degradation is higher or lower, the glass transition temperature of the outer shell of the microcapsules is provided accordingly.

[0119] It is known that the glass transition temperature of a polymer is tunable to some extent by proper selection of polymer molecular weight and other properties. In one embodiment, the nano/macrocapsules of the lubricant additive consist essentially of parylene polymer, preferably parylene C, also known as Di-chloro-di-p-Xylylene, as described in Parylene Conformal Coatings Specifications and Properties, published by Specialty Coating Systems, Inc., 1992, and the document available at http://www.scoolkson.com/nos/docs/coatspec.pdf by downloading.

[0120] In the operation of an internal combustion engine, there occurs some direct metal-to-metal contact in the engine, by the sliding action of the piston rings (and to some extent the piston skirts) in the cylinder bores. Such metal to metal contact can provide sufficient shear and/or crushing action to rupture the nano/macrocapsules, such that a gradual change in oil color is provided by the lubricant indicator. In one embodiment, the lubricant indicator is provided with a concentration and color change capability that indicates over a long period of normal operation the breakdown of the lubricant oil, if no extremes of shear or temperature are encountered during the period of operation. Such a capability is also useful in the use of the indicating lubricant in a cutting oil, where direct metal-to-metal contact occurs by design.
In another embodiment, the indicating capsules in the lubricant additive are formed by nanotubules or microtubules. A micro- or nanotubule is a cylindrical hollow tube that can be filled with dyes or reactive reagents and subsequently suspended in a fluid. Carbon nanotubes are one known form of tubule that has been filled with a variety of elements such as hydrogen, lithium, liquid silver to fullerences. For example, one may refer to U.S. Pat. No. 6,591,617 of Wolfe, “Method and apparatus for hydrogen storage and retrieval,” U.S. Pat. No. 6,672,077 of Bradley et al., “Hydrogen storage in nanostructure with phase transition,” U.S. Pat. No. 6,762,331 of Hong et al., “Synthesis of organic nanotubes and synthesis of ultrathin nanowires using same as templates,” and in U.S. Pat. No. 6,437,329 of Yedur et al., “Use of carbon nanotubes as chemical sensors by incorporation of fluorescent molecules within the tube,” the disclosures of which are incorporated herein by reference. One may also refer to the publication of Dillon et al., “Storage of hydrogen in single-walled carbon nanotubes,” Nature, vol. 386, Mar. 27, 1997, pp. 377-379.

In one embodiment, nanotubules, such as e.g., single walled carbon nanotubes (SWNT), or multiwalled carbon nanotubes (MWCNT) are filled with dye or synthesized with dye therein, and suspended in a carrier fluid for the lubricant additive such as e.g. a hydrocarbon or mineral oil that is miscible with the lubricant oil for which an indication of the condition is sought. At time zero, the lubricant additive is then added to the lubricant oil, such as e.g. to the crankcase of an IC engine. In use, the dye contained in the nanotubules is then discharged therefrom, thereby changing the color of the lubricant and indicating a degree of use thereby. The transport mechanisms by which the dye is discharged from such nanotubules include convection and diffusion. Such transport may be further limited and/or regulated by the phenomenon of adsorption of the dye on the inner walls of the nanotubules.

In the case of transport by diffusion (and desorption if applicable), the rate of such transport is dependent to a large extent upon temperature. Thus, if the lubricating oil is exposed to a destructive high temperature, the dye is rapidly discharged from the nanotubes, indicating degradation of the lubricant. In a preferred embodiment, a dye is chosen that provides highly saturated color, so that a relatively small concentration in the lubricant is needed in order to provide an indication. In this manner, the concentration gradient that drives diffusion of dye from within the nanotubes is maintained at a high level, and the concentration of dye present in the oil will have substantially no effect on the rate of further release. It will be apparent that tubule diameter is a critical parameter for controlling the rate of diffusion of dye therefrom. Depending on the tubule type and the size and chemistry of the dye, the optimum diameter of such tubules will vary. In general, it is preferable that such tubules have an internal diameter of between about 3 nanometers and about 500 nanometers.

In the case of transport by convection, the rate of such transport is dependent to a large extent upon the shear forces that are present in the application. Since the nanotubes are provided with some degree of flexibility, such nanotubes are deformed when exposed to high localized shear, thus displacing dye from within. As described previously, such high shear is present and at highest levels in areas of surface motion where the lubricant gap is at a minimum, which results from the degradation of the lubricant. Thus the displacement of indicating dye from the nanotubes is an indication of the degradation of the lubricant. Such high shear may bend and/or compress the tubules, thereby convectively forcing the dye out therefrom, analogous to the displacement of toothpaste or ointment from a tubular package. In a further embodiment, the high shear fractures the tubules, thereby releasing the dye as in the microcapsule embodiment previously described.

Although the preferred lubricant indicating material contained in a microcapsule or microtubule is a dye, the present invention is not limited to formulation exclusively with only dyes being provided within such tubules or capsules. Other microcapsule or microtubule contents could include pigments, lubricants, nanoparticle lubricants, environmentally friendly remediation agents, or active “reagents” to clean or refresh the lubricant oil. Other carrier fluids could include inks, sol-gel products (arogels, zergels), water, etc., further incorporating dissolved gases. While the principal adverse conditions that cause the color change in the lubricant indicator are shear stress and thermal stress, other physical stresses or agents that could cause indicating changes, i.e. microcapsules to break apart or nanotubules to bend include the presence of dirt, chemical contaminants, and a change in lubricant viscosity or chemical composition. In lubricant additive formulation, suspension of the microcapsule/tubules in the additive carrier could include dissolution techniques, emulsion techniques, etc.

In another embodiment, the indicating lubricant additive contains dendritic polymer as previously described in this specification and shown in FIGS. 2-4. FIG. 7A is a schematic representation of the presence of dendritic polymers in a lubricant gap greater than the minimum allowable lubricant gap, and FIG. 7B is a schematic representation of the removal of an outer layer of a dendritic polymer capsule by the shearing and/or crushing action thereof in a lubricant gap that is less than the minimum allowable lubricant gap. Referring to FIG. 7A, parts 802 and 804 are separated by an acceptable lubricant gap 989, and dendritic polymer molecules 600 having outer layer 602 are entrained within the high shear flow field of lubricant 70 therebetween.

Referring now to FIG. 7B, as lubricant 70 undergoes degradation during use, and the lubricating properties thereof diminish, the lubricant gap between parts 802 and 804 decreases, to an unacceptable gap 988. Under this circumstance, dendritic polymer molecules 600 are compressed in gap 988, and the shearing and/or crushing action between parts 802 and 804 removes outer layer or generation 602 as indicated by fragments 606, resulting in molecules 600 with former intermediate layer 604 now the exterior layer thereof mixed into lubricant 70. Such molecules with layer 604 on the exterior thereof result in a color change of lubricant 70, indicating that such lubricant is failing. Such indication occurs before lubricant gap becomes zero, i.e. before contact of parts 802 and 804 occurs, thus providing a warning before catastrophic failure of such parts occurs.

It will be apparent that dendritic polymer may have any of the structures of the dendritic polymers 100, 200, and/or 300 that are depicted in FIGS. 2-4. It will be further apparent that in this application, the lubricant gaps that result
in the change in the dendrimers are much smaller than in the applications of FIGS. 6A and 6B, as the diameter of such dendrimers is on the order of 50-100 Angstroms (5-10 nanometers). Thus the application illustrated in FIGS. 7A and 7B is best suited to lubrication of parts having extremely close running clearances, or in cutting applications.

[0129] In some embodiments of use of the lubricant indicator of the present invention, such indicator is read or judged visually by a human. In one embodiment provided for use with an IC engine, or other device having a lubricant dipstick, there is provided a color coded or calibrated rag that is used to wipe such dipstick, or in a grinding application, the part that is being ground, or the tool that is performing the material removal from the ground part. A color scale is printed or otherwise affixed to the rag, and based on a visual comparison of such color scale with the color of the lubricant, the user can determine if the lubricant oil is approaching failure and needs to be changed.

[0130] In one embodiment, for example, a white rag with a label having a portion of the color spectrum from bright (i.e. relatively high hue, saturation, and luminance) yellow, to bright orange, to bright red is used to wipe off the dipstick of an engine in a car using oil containing the lubricant additive of the present invention. The user visually compares the color of the oil wiped on the rag to the scale to determine how degraded the oil is. In the preferred embodiment, a reading of the scale indicates to the user that at a particular color of oil it is time to get the oil in the engine changed. In a further embodiment, the rag is specially treated to enhance color distinction (brightness and/or contrast) or to react to the color changing agent to make the need for an oil change easier to determine.

[0131] In further embodiments, other agents that the rag could be used to detect through pretreatment thereof with the appropriate chemicals and binders include pigments, lubricants, nanoparticle lubricants, presence of dirt, contaminate, and/or a change in lubricant viscosity or chemical composition. Appearance changes of rag in response to such agents include visible color, texture, and/or IR spectrum, the latter requiring additional detection instrumentation.

[0132] In a further embodiment, there is provided an engine dipstick that measures the color change in the oil and relays that information to an on-board computer system. Such a dipstick is preferably used with a lubricant containing an indicating lubricant additive of the present invention. However, the use of such a dipstick is not limited to measurement of oils containing such an indicating additive.

[0133] FIG. 8 is a schematic representation of a cross-sectional view of an internal combustion engine having a sensing dipstick for detecting the color change of a lubricant oil during use thereof, and FIG. 9 is a cross-sectional view of a general embodiment of the sensing dipstick of FIG. 8, comprising sensor means for sensing at least one property of the lubricant oil with which it is in contact. Referring to FIG. 8 and FIG. 9, and in one embodiment depicted therein, sensing dipstick 700 is housed in a housing tube 776 that is disposed in the lower portion of block 777 of engine 770.

[0134] Sensing dipstick 700 comprises a handle 704, electronic circuit housing 706, an elongated body 702, and sensing means 720 disposed at the distal end 701 thereof. Handle 704 may be ring-shaped as depicted in FIG. 9, and joined to circuit housing 706 by a short rod 705, although many other configurations that are ergonomically suitable for engagement with the fingers of a hand may be suitable. Elongated body 702 is preferably a hollow tubular body, in which is disposed signal transmission means 710, which transmit sensed signals and/or data from sensing means 720 to electronics housing 706.

[0135] In circumstances where such sensed signals and/or data are electrical signals, transmission means 710 comprises electrical conductors, e.g., wires, and may further include electromagnetic shielding of such wires, e.g., foil or a suitable coating. In circumstances where such sensed signals are optical signals, i.e., light, transmission means 710 comprises at least one optical fiber. Signals from sensing means 720 are transmitted to electronic/electro-optic circuit board 707 that is disposed within circuit housing 706. Such signals are further processed and/or analyzed, and then such processed signals and/or analytical data are then transmitted to remote processor 752. Circuit board 707 further comprises a suitable power supply, such as e.g., battery 709. Such battery 709 is preferably a compact, high energy density battery such as, e.g., a lithium polymer battery. In another embodiment (not shown), power may be supplied from the main vehicle battery through suitable wiring and a connector, such as a flexible cable cord and electrical quick disconnect plug and receptacle.

[0136] Remote processor 752 may be an on-board computer which acquires and analyzes vehicle data, controls engine 770, and/or sends warnings via e.g., dashboard displays, to the vehicle operator. Alternatively, remote processor may be a computer separate from the vehicle, e.g., a vehicle analyzer that is used in a vehicle service shop. In the preferred embodiment, communication between sensing dipstick 700 and remote processor 752 is wireless communication, such as via radio frequency transmission from antenna 708 on sensing dipstick 700 to antenna 754 on remote processor 752.

[0137] In one embodiment, sensing dipstick 700 further comprises indicia and/or marks 749 and 748 for the typical function of indicating oil level. In another embodiment, sensing means 720 is provided with the capability of sensing in oil pan 772 the level of the oil on dipstick 700, as well as a property of oil 70. In another embodiment, sensing means 720, housing 702, and other surfaces of sensing dipstick 700 that are wetted by lubricant oil 70 and/or exposed to adverse environmental conditions near engine 770 are coated with a protective insulating conformal coating such as paralene, a poly-(para-xylene) polymer, or other suitable film coating.

[0138] FIG. 10 is a cross-sectional schematic view of an embodiment of the sensing dipstick of FIG. 9, wherein the lubricant property sensor means thereof senses the color of such lubricant oil. For the sake of clarity of illustration, a substantial portion of the elongated body 702 of sensing dipstick 700 is not shown, so that the distal end 701 and the proximal end 751 thereof may be shown enlarged and in greater detail. Referring to FIG. 10 and FIGS. 8 and 9, light is transmitted to sensing means 720 from a suitable light source such as, e.g., an ultrabright light 799 emitting diode 703 located on circuit board 707, through transmission means 710 comprised of an optical fiber or fiber bundle 711.
In another embodiment (not shown), the light source may comprise separate red, blue, and green light emitting diodes, so that the RGB color measurements of the oil may be made.

[0139] Sensing means 720 further comprises flow cell 722 disposed within housing 702. Flow cell 722 comprises an internal passageway 724, through which flows oil 70 (see FIG. 8) to be measured. Passageway 724 also provides an optical pathway for the exposure of oil 70 to light 799. In the embodiment depicted in FIG. 10, such pathway is transmissive, wherein light 799 is directed into passageway 724, and subsequently emerges as transmitted light 798 from passageway 724 into a second optical fiber 713. In another embodiment (not shown), such pathway may be reflective, wherein light 799 is directed into passageway 724 to a reflective characterization thereof, and reflected light returns back, through optical fiber 711, where it is directed to measurement means to be described subsequently herein. In another embodiment, the wetted surfaces of the passageway 724 of flow cell 722 are coated with a thin film of high surface energy material to prevent adhesion and fouling of such surfaces with various constituents in the oil.

[0140] For the sake of simplicity of illustration, in the embodiment depicted in FIG. 10, the optical pathway through passageway 724 through which light 799 is transmitted is shown to be a large portion of the length of passageway 724. It is to be understood that in the preferred embodiment, the optical pathway of light through passageway 724 is substantially perpendicular to the longitudinal axis of passageway 724, so that light 799 is directed through a thin flowing film of oil, perpendicular to such flow direction. Configuring a flow cell and a light source such that light is transmitted or reflected through a thin flowing fluid film in order to enable measurements of properties of such flowing fluid is described in U.S. Pat. No. 6,195,443, “System using on-line liquid characterization apparatus” of Hammond et al., the disclosure of which is incorporated herein by reference.

[0141] Referring again to FIG. 10, sensing dipstick 700 further comprises spectrometer analyzer 730 having photo detector 731 disposed within circuit housing 706. In one embodiment, spectrometer analyzer 730 comprises a mini-infraredometer for detection of the wavelength(s) of light 798. In another embodiment, spectrometer analyzer 730 comprises a monochromator. Spectrometer analyzer 730 may further comprise light source 703 integrated therein to supply light 799 to sensing means 720.

[0142] In one embodiment (not shown), sensing dipstick 700 is provided with a passageway entrance along the housing 702 such that when the motor 770 (see FIG. 8) is in operation, the rotating crankshaft 779 of such motor pumps and/or flings motor oil 70 against housing 702 of dipstick 700 such that the oil passes through the passageway 724 of flow cell 722 in a substantially continuous manner. In the embodiment depicted in FIG. 10, sensing dipstick 700 is further provided with a micropump 740 that delivers oil from inlet 741 through flow cell 722 and out through outlet 742 in housing 702. In a further embodiment, micropump 740 is further provided with means for selecting liquid contained in a reservoir 744 and delivering such liquid through flow cell 722. Such liquid, in one embodiment, is clean lubricant oil that is used to flush out flow cell 722 and/or calibrate spectrum analyzer 730.

[0143] In a further embodiment, the power that is supplied through wiring (not shown) to pump 740 is monitored, such power providing an indication of the load that is on pump 740, and thus providing an indication of the viscosity of the sampled lubricant oil being displaced by pump 740.

[0144] Examples of suitable micropumps, and fabrication methods and suitable materials of fabrication may be found e.g., in U.S. Pat. No. 6,752,601 of Takeuchi et al., “Micropump,” U.S. Pat. No. 6,677,190 of Cabuz et al., “Methods of operating an electrostatically actuated pump,” U.S. Pat. No. 6,761,962, of Bentsen et al., “Microfluidic articles,” U.S. Pat. No. 6,743,636 of Chung et al., “Microfluid driving device,” and in U.S. Pat. No. 6,716,002 of Hagashino, “Micropump,” the disclosures of which are incorporated herein by reference.

[0145] In a further embodiment, sensing dipstick is provided with microfluidic channels 746 within housing 702 to spread and thin the oil sample to be measured prior to the flow thereof through flow cell 722. In such an embodiment, it is preferred to dispose micropump 740 downstream from flow cell 722 or upstream from such channels 746, so that the oil flows from such channels directly into flow cell 722. In one embodiment (not shown), micropump 740 is disposed within circuit housing 706, with the inlet and outlet fluid conduits thereof directed from the distal end 701 of sensing dipstick 700 to pump 740, and back to flowcell 722. Such microchannels may further comprise resistive heaters to reduce the viscosity of the oil sample, thereby facilitating the flow of oil 70 through sensing means 720.

[0146] Examples of such microfluidic channels and heaters, and fabrication methods and suitable materials of fabrication may be found e.g., in U.S. Pat. No. 6,727,479 of Villa et al., “Integrated device based upon semiconductor technology, in particular chemical microreactor,” U.S. Pat. No. 6,232,150 of Lin et al., “Process for making microstructures and microstructures made thereby,” U.S. Pat. No. 4,696,188 of Higashi, “Semiconductor device microstructure,” and in U.S. Pat. No. 6,749,814 of Bergh et al., “Chemical processing microsystems comprising parallel flow microreactors and methods for using same,” the disclosures of which are incorporated herein by reference.

[0147] In operation, spectral analyzer 730 provides signal conditioning and analysis of light 798 to determine the color of the oil 70, with such color being indicative of the lubricating properties of the oil as described previously herein. The data/analysis information from spectrum analyzer 730 is communicated to RF/wireless transceiver 747, which then transmits such data via radio frequency transmission from antenna 708 on sensing dipstick 700 to antenna 754 on remote processor 752 (see FIG. 8) as described previously. Transceiver 747 is also capable of receiving transmitted data from and external source.

[0148] In one embodiment of operation of engine 770 and sensing dipstick 700, when engine 770 is turned on or off, sensor means 720 of dipstick 700 takes a measurement of light that is transmitted through or back-reflected from the oil 70, and sends that spectral data back to either the on-board computer 750 in the car, or a remotely located off-board receiver 750 dedicated for such purpose. The spectrum is then analyzed, comparing it to previous results as well as standard spectrum ranges that are known to indicate the condition of the oil containing the lubricant additive of the present invention, and the computing unit 750 determines whether the results are within accepted limits. If
so, the data is stored for the next comparison. If not, the computer warns the driver to get an oil change through various communications media provided in the vehicle (such as a dashboard display), and stores the data for later use.

[0149] This preferred method of lubricant sensing enables early diagnosis of engine malfunction and analysis of engine failure, by providing an archived means of monitoring engine wear over time. It is to be understood that in the foregoing description, the present invention is referred to as a sensing dipstick. However, the present invention is not limited to being used as a dipstick that is removed and replaced in the lubricant oil as is done with a simple dipstick. The sensing means of the present invention may be provided in other configurations and installed in such a manner as to be in contact with the lubricant oil to be monitored. Such contact may be by continuous immersion in a vessel or in a pipe having flow therethrough, or intermittent contact by mechanical action such as splashing.

[0150] In a preferred embodiment, dipstick sensor 700, and particularly any electrical components thereof, are electrically isolated so as to prevent any spark, short circuit, or other energy discharge that could result in ignition of oil of flammable vapors present. In a further embodiment, the user (e.g., driver or mechanic) may input the color-changing or normal oil type to calibrate the oil sensing dipstick with the known standards indicative of desired oil properties.

[0151] FIG. 11 is a cross-sectional view of a further embodiment of the sensing dipstick of FIG. 9 and FIG. 10, wherein the lubricant property sensor means thereof senses conductivity and/or pH and/or rheological properties of such lubricant oil. For the sake of clarity of illustration, a substantial portion of the elongated body 702 of sensing dipstick 800 is not shown, so that the distal end 701 and the proximal end 751 thereof may be shown enlarged and in greater detail. Referring to FIG. 11, sensing dipstick 800 comprises many of the same components as described for sensing dipstick 700 of FIG. 10. For the sake of simplicity of illustration, spectrum analyzer 730, optical fibers 711 and 713, and certain details of flow cell 722 are not shown in FIG. 11, with it being understood that such components are included in sensing dipstick 800 of FIG. 11.

[0152] Sensing dipstick 800 further comprises a conductivity and/or pH sensor 810 preferably disposed downstream from passageway 724 of flow cell 722. Conductivity/pH sensor 810 further comprises a reservoir or bulb 812 containing a reference electrolyte 814 of known standard ion concentration with known conductivity that is separated from flowing sample 725 by membrane 816, such that diffusion across such membrane 816 causes pressure within bulb 812 and/or pH within reservoir 812 to change. A difference in ion concentration or conductivity causes diffusion across membrane 816, and a pressure change of the bulb which is detected and related to the relative ion concentrations. Such a sensor 810 may be “on” all the time and send an alert anytime the results are out of a set range, or such a sensor 810 may turn on everytime the engine 770 starts or stops (the preferred process being the one that provides a fresher sample of lube to sensor 810). Intermittent use of sensor 810 may be better than continuous use, which may limit the life cycle of sensing dipstick 800 as reference solution 814 ages or leaches into oil 70. If intermittent use is the preferred mode of operation, there is further provided, a “housing cap” (not shown) that is easy to remove and replace. Such housing cap is included to protect the sensing dipstick 800; or in another embodiment, the dipstick 800 can extend during measurement and retract thereafter.

[0153] Examples of microsensing devices and/or systems, and fabrication methods and suitable materials of fabrication thereof may be found e.g., in U.S. Pat. No. 6,705,152 of Routkevitch et al., “Nanostructured ceramic platform for micromachined devices and device arrays,” U.S. Pat. No. 6,286,363 of Discenzo, “Integrated multi-element lubrication sensor and health lubricant assessment system,” and U.S. Pat. No. 6,602,714 of Tagge et al., “Viscosity and mass sensor for the high-throughput synthesis, screening and characterization of combinatorial libraries,” the disclosures of which are incorporated herein by reference.

[0154] Sensing means 720 of sensing dipstick 800 preferably further comprises a small flushing reservoir 743 from which is drawn by pump 740 clean lubricant oil that is used to flush out sensor 810 and passage 724 of flow cell 722. Reservoir 743 is provided with self-filling capability that is actuated after every oil change.

[0155] Referring again to FIG. 11, in a further embodiment, sensing dipstick 800 further comprises a reservoir 844 disposed in housing 706 and connected to an outlet 846 by fluid conduit 848. Reservoir 844 may contain additional indicating lubricant additive to be released into oil 70 in pan 722, or reservoir 844 may contain other useful agents such as e.g., environmental remediation means that breaks down oil 70 just prior to an oil change.

[0156] Dipstick sensing means may further include those means that are capable of infrared spectral detection/analysis, compositional testing, heat stability or viscosity, etc. The communication means to the on-board computer may be direct or wireless using radio frequency (RF) signals, infrared signals, etc. In further embodiments, the sensor could be a single sensing unit or a series of sensors distributed along or otherwise embedded within the dipstick. The sensing dipstick device may be powered by any suitable power supply, such as a battery, thermoelectric, microcantilever vibrations, microfuel cells, or an inductively coupled or RF source provided externally. Depending upon the parameter being sensed, the sensing means may either measure a sample of the lubricant oil or may make a direct measurement of the bulk oil. It will be apparent that such a sensing apparatus is also applicable to sensing the condition of other automotive fluids and systems, such as coolant systems, and fuel systems.

[0157] It is, therefore, apparent that there has been provided, in accordance with the present invention, an indicating lubricant additive composition for addition to a lubricant to enable indication of the lubricating properties thereof, and a lubricant sensing dipstick comprising sensor means for sensing at least one property of the lubricant oil with which it is in contact. While this invention has been described in conjunction with preferred embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.
We claim:

1. An indicating lubricant additive comprising a color-changeable polymer comprising an outer layer of a first color, and a first intermediate layer of a second color.

2. The indicating lubricant additive as recited in claim 1, wherein said color changing polymer is a dendritic polymer.

3. The indicating lubricant additive as recited in claim 2, wherein said first intermediate layer is comprised of a first dye.

4. The indicating lubricant additive as recited in claim 3, wherein said outer layer is opaque.

5. The indicating lubricant additive as recited in claim 3, wherein said outer layer masks the color of said intermediate layer.

6. The indicating lubricant additive as recited in claim 3, wherein when said lubricant additive is mixed with a lubricant, said outer layer is removable by an effect selected from the group consisting of dissolution, etching, abrasion, fracturing and shedding, and combinations thereof.

7. The indicating lubricant additive as recited in claim 3, wherein said outer layer is comprised of a second dye.

8. The indicating lubricant additive as recited in claim 3, wherein said first dye is a yellow dye.

9. The indicating lubricant additive as recited in claim 8, wherein said yellow dye is a dicyanoalanine dye.

10. The indicating lubricant additive as recited in claim 2, wherein said dendritic polymer is a poly(amideamine) polymer.

11. The indicating lubricant additive as recited in claim 10, wherein said outer layer consists essentially of hexamidine.

12. The indicating lubricant additive as recited in claim 10, wherein said dendritic polymer is of at least about six generations.

13. The indicating lubricant additive as recited in claim 2, further comprising a second intermediate layer of a third color.

14. The indicating lubricant additive as recited in claim 13, wherein said second intermediate layer comprises a third dye.

15. The indicating lubricant additive as recited in claim 1, wherein said color changeable polymer is distributed throughout a fluid carrier.

16. A lubricant composition comprising a carrier, a particular metal alloy selected from the group consisting of copper-nickel-tin, copper-nickel-tin-zinc and mixtures thereof, said particular metal alloy having a first color and being dispersed in said carrier, and an indicating lubricant additive comprising a color-changeable polymer comprising an outer layer of a second color, said second color of said lubricant additive masking said first color of said particular metal alloy.

17. The lubricant composition as recited in claim 16, wherein said color changing polymer is a dendritic polymer.

18. The lubricant composition as recited in claim 17, wherein said outer layer of said color changing polymer is comprised of a dye.

19. The lubricant composition as recited in claim 18, wherein said dye is a yellow dye.

20. The lubricant composition as recited in claim 19, wherein said yellow dye is a dicyanoalanine dye.

21. The lubricant composition as recited in claim 17, wherein said dendritic polymer is of at least about six generations.

22. A lubricant additive for indicating the condition of a lubricant composition including a carrier and a particular metal alloy selected from the group consisting of copper-nickel-tin, copper-nickel-tin-zinc and mixtures thereof, said particular metal alloy having a first color and being dispersed in said carrier, said lubricant additive comprising a color-changeable polymer comprising an outer layer of a second color, said second color of said lubricant additive masking said first color of said particular metal alloy when said lubricant additive is mixed with said lubricant composition.

23. The lubricant additive as recited in claim 22, wherein said color changing polymer is a dendritic polymer.

24. The lubricant additive as recited in claim 23, wherein said outer layer of said color changing polymer is comprised of a dye.

25. The lubricant additive as recited in claim 24, wherein said dye is a yellow dye.

26. The lubricant additive as recited in claim 25, wherein said yellow dye is a dicyanoalanine dye.

27. The lubricant additive as recited in claim 23, wherein said dendritic polymer is of at least about six generations.

28. An indicating lubricant additive comprising a fluid carrier, a plurality of microcapsules comprised of shell walls defining interiors within said microcapsules, and a dye disposed within said interiors of said microcapsules.

29. The indicating lubricant additive as recited in claim 28, wherein said dye is a red dye.

30. The indicating lubricant additive as recited in claim 28, wherein said dye is a yellow dye.

31. The indicating lubricant additive as recited in claim 30, wherein said yellow dye is a dicyanoalanine dye.

32. The indicating lubricant additive as recited in claim 28, wherein said microcapsule is fractureable by fluid shear.

33. The indicating lubricant additive as recited in claim 28, wherein said shell walls of said microcapsules totally enclose said interiors within said microcapsules.

34. The indicating lubricant additive as recited in claim 33, wherein said microcapsules are substantially spherical in shape.

35. The indicating lubricant additive as recited in claim 34, wherein said microcapsules are between about 6 micrometers and about 15 micrometers in diameter.

36. The indicating lubricant additive as recited in claim 34, wherein said microcapsules are between about 0.05 micrometers and about 0.5 micrometers in diameter.

37. The indicating lubricant additive as recited in claim 33, wherein said shell walls of said microcapsules consists essentially of a lipid.

38. The indicating lubricant additive as recited in claim 33, wherein said shell walls of said microcapsules consists essentially of a polymer.

39. The indicating lubricant additive as recited in claim 38, wherein said polymer is paraffin polymer.

40. The indicating lubricant additive as recited in claim 28, wherein said shell walls of said microcapsules are nanotubes each having a first end and a second end, and wherein at least one of said first end and said second end is an open end.

41. The indicating lubricant additive as recited in claim 38, wherein said nanotubes are carbon nanotubes.

42. The indicating lubricant additive as recited in claim 38, wherein said nanotubes are between about 3 nanometers and about 500 nanometers in length.
43. A lubricant composition comprising a carrier, a particulate metal alloy selected from the group consisting of copper-nickel-tin, copper-nickel-tin-zinc and mixtures thereof, said particulate metal alloy having a first color and being dispersed in said carrier, and an indicating lubricant additive comprising a fluid carrier, a plurality of microcapsules comprised of shell walls, said shell walls defining interiors within said microcapsules and comprising a first colored dye, and a second colored dye disposed within said interiors of said microcapsules, wherein said first colored dye of said lubricant additive masks said first color of said particulate metal alloy.

44. The lubricant composition as recited in claim 43, wherein said first colored dye is a red dye.

45. The lubricant composition as recited in claim 43, wherein said first colored dye is a yellow dye.

46. The lubricant composition as recited in claim 45, wherein said yellow dye is a dicyanoamine dye.

47. The lubricant composition as recited in claim 43, wherein said microcapsule is fracturable by fluid shear.

48. A lubricant additive for indicating the condition of a lubricant composition including a carrier, a particulate metal alloy selected from the group consisting of copper-nickel-tin, copper-nickel-tin-zinc and mixtures thereof, said particulate metal alloy having a first color and being dispersed in said carrier, said lubricant additive comprising a fluid carrier, a plurality of microcapsules comprised of shell walls, said shell walls defining interiors within said microcapsules and comprising a first colored dye, and a second colored dye disposed within said interiors of said microcapsules, wherein said first colored dye of said lubricant additive masks said first color of said particulate metal alloy when said lubricant additive is mixed with said lubricant composition.

49. The lubricant additive as recited in claim 48, wherein said first colored dye is a red dye.

50. The lubricant additive as recited in claim 48, wherein said first colored dye is a yellow dye.

51. The lubricant additive as recited in claim 50, wherein said yellow dye is a dicyanoamine dye.

52. The lubricant additive as recited in claim 48, wherein said microcapsule is fracturable by fluid shear.

53. A lubricant sensing dipstick comprising an elongated body having a proximal end and a distal end, a circuit housing joined to said proximal end of said elongated body, and lubricant sensing means disposed at said distal end of said elongated body.

54. The lubricant sensing dipstick as recited in claim 53, further comprising a handle.

55. The lubricant sensing dipstick as recited in claim 53, wherein said elongated body is a hollow tubular body.

56. The lubricant sensing dipstick as recited in claim 55, wherein said circuit housing comprises a remote processor.

57. The lubricant sensing dipstick as recited in claim 56, wherein said circuit housing further comprises a transceiver and an antenna for transmitting and receiving radio transmitted data.

58. The lubricant sensing dipstick as recited in claim 56, wherein said circuit housing further comprises an electrical power supply.

59. The lubricant sensing dipstick as recited in claim 56, further comprising signal transmission means disposed within said hollow tubular body, said signal transmission means providing communication between said circuit housing and said lubricant sensing means.

60. The lubricant sensing dipstick as recited in claim 59, wherein said signal transmission means is electrical signal transmission means.

61. The lubricant sensing dipstick as recited in claim 59, wherein said signal transmission means is optical signal transmission means.

62. The lubricant sensing dipstick as recited in claim 61, wherein said circuit housing further comprises a light source.

63. The lubricant sensing dipstick as recited in claim 62, wherein said circuit housing further comprises light measurement means.

64. The lubricant sensing dipstick as recited in claim 63, wherein said light measurement means is a spectrum analyzer.

65. The lubricant sensing dipstick as recited in claim 63, wherein said sensing means comprises a flow cell.

66. The lubricant sensing dipstick as recited in claim 65 wherein said sensing means further comprises at least one fluid channel in communication with said flow cell.

67. The lubricant sensing dipstick as recited in claim 66, wherein said sensing means further comprises a micropump in communication with said at least one fluid channel.