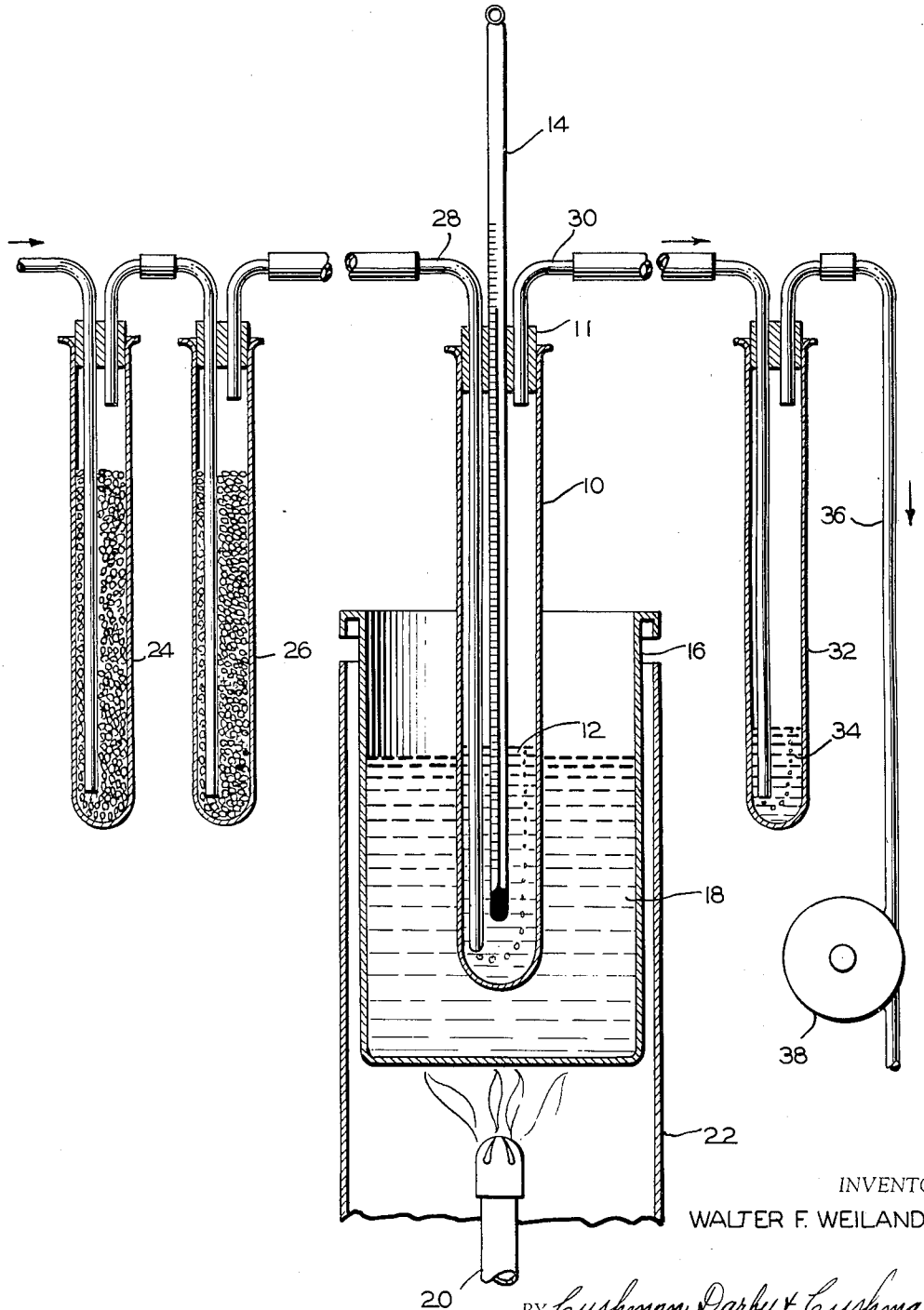
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PROCESS FOR DETERMINING ACID OR ACID-VAPOR FORMATION CHARACTERISTICS OF A SUBSTANCE

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PROCESS FOR DETERMINING ACID OR ACID-VAPOR FORMATION CHARACTERISTICS OF A SUBSTANCE

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This invention relates to a method for accurately determining the temperature at which a substance, either liquid or solid, can be expected to liberate vapors of a corrosive or acid nature, either through oxidation or cracking or from the inherent nature of the material. In its broader aspects the process and apparatus of the present invention also may be used to determine the pH of vapors liberated from a substance under the influence of heat. More particularly, this invention is adapted for determining the acid or acid-vapor formation characteristics of a substance such as oils, greases and gases.

The stability of oils, and in particular lubricating oils, has been a vital problem for many years. First attempts to evaluate stability led to the development of a number of oxidation tests, such as the Indiana test and the Sligh test.

No oxidation test has ever proven to be adequate to evaluate all problems related to oil stabiltiy. These tests give no specific or direct information on the corrosive properties of the products of oil breakdown. It has been reasoned by those skilled in the petroleum art that vapors are probably liberated by a lubricating oil under conditions of elevated temperature and service, and that these vapors have a deleterious effect on bearing metals and other metal parts.

Reactions in internal combustion engines are varied, complex and uncertain. Lubricating oil temperatures range from 220° F. in the oil sump on a warm day to 300° F. in the bearings and 400 to 500° F. at the ring belt. Oil is whipped around as a mist in the crank case and in this manner adsorbs considerable quantities of air. This adsorbed air serves to increase the rate of oil breakdown by at least three times when the oil is subjected to heat and pressure in the bearings and at the ring belt.

Lubricating oils, being hydrocarbons, are, under the conditions enumerated above, subject to oxidation. However, the breakdown process is necessarily very complex, and the order of events and the intermediate reactions produced depend on such factors as the structure of the original oil molecule, the temperature, pressure, presence of air, carbon monoxide, carbon dioxide, metallic catalyst and others. Such a combination of factors introduces a considerable element of uncertainty into any speculation about the nature of intermediate products.

The step-by-step oxidation might be illustrated by the progressive breakdown of a sample hydrocarbon such as methane:

Methane→methyl alcohol→aldehyde→

$CH_4 \rightarrow CH_3OH \rightarrow HCHO \rightarrow$

Formic acid→carbonic acid

$HCHO_2 \rightarrow H_2CO_3$

Each addition of oxygen is a partial combustion reaction and is, therefore, exothermic. The heat generated in each stage is absorbed in part, at least, by the molecule undergoing degeneration. The result is a rise in temperature of the molecule and an acceleration of

further reactions. This may mean partial cracking if the reaction is going on in larger molecules and the formation of methane, ethane, and other like hydrocarbons which are held in solution to more or less limited extent in the lubricating oil. The step-by-step oxidation will then proceed about as previously indicated for methane.

Ventillation of the crank case to remove the volatile acids is of no material advantage, because the damage appears to be done when the acids form, which is considerably before they can be freed from the oil. The corrosive effect of degraded lubricating oils on the metal parts of internal combustion engines and other metal surfaces coming in contact with such oils is of considerable concern to automotive engineers and others concerned with this problem.

A new lubricating oil is composed of much larger molecules than indicated by methane, and upon initial oxidation, the higher aldehydes and acids, which may be said to be less harmful, form first. If progressive degeneration of the oil occurs, the lower, more corrosive acids make their appearance.

It is, therefore, a principal object of the present invention to provide a method and apparatus for determining the temperature at which a substance may be expected to either oxidize or break down under the influence of heat to yield acid vapors.

It is a further object to provide a means for giving specific and direct information as to the corrosive properties of the products of oil breakdown.

A still furhter object is to provide a method and apparatus which may be used in connection with any substance, whether liquids, semi-solids or solids, wherein the hydrogen ion concentration of the vapors liberated from the substance under the influence of heat may be ascertained.

The invention will be better understood by reference to the accompanying drawing showing a detailed illustration of the improved apparatus used in accordance with the present invention and in connection with which the invention will be described.

While, as previously mentioned, the invention may be used to determine the acid or alkaline vapor characteristics of any substance which is either oxidized under the influence of heat to yield low boiling acids, or which contains acids or bases initially, the invention will be described in connection with the testing of a sample of lubricating oil to ascertain the acid properties of the products of oil breakdown.

The extent of oil breakdown can be determined by measuring the temperature at which volatile acids form. This may be readily accomplished by passing the vapors from the oil through a sensitive indicator as the oil is slowly heated and noting the temperature of the oil at which the indicator changes. Accurate and consistent results are possible when proceeding in the manner to be hereinafter described. The temperature at which acid vapors are first liberated is defined according to the present invention as the "acid vapor temperature" of the oil or substance being tested.

The acid vapor temperature of new lubricating oils ranges from 250 to 330° F. depending on the oil and the additives in the oil. If the oil is oxidized either by laboratory methods or on the road, acid vapor temperature gradually drops to a low of under 100° F. The oil in this latter condition has long since passed its useful life.

It should be emphasized that the acid vapor temperature need not indicate the presence of free acids in the oil. It is, however, an indication of the temperature at which volatile acids form, and when this temperature drops to a rather definite point, it is an indication of incipient corrosion. For example, a lubricating oil must be considered as having approached the end of its use-

ful life when its acid vapor temperature drops to 215° F.

According to the present invention, in order to determine the temperature at which volatile acids form and the temperature at which incipient corrosion of metal surfaces in contact with such an oil may be expected, a sample of the oil to be tested is placed in a suitable container such as the test tube **10**, shown in Figure 1, which is provided with a three holed stopper **11**. A thermometer **14** is inserted into the container **10** through stopper **11** so that it extends well into the sample **12** but without touching the walls of the container **10**. The container **10** may be immersed into a second container **16** containing a suitable oil bath **18** or other heat transfer medium. A Bunsen burner **20** or other source of heat is placed beneath container **18** and the source of heat and container **18** are protected from air currents by means of the sleeve device **22**.

Air, oxygen or any other suitable gas or vapor, either singly or in desired proportions and hereinafter designated as "air" is conducted through the air washing, drying and cleaning containers **24** and **26**. The containers **24** and **26** may be filled with silica gel for drying the air and sodium calcium hydrate for removal of carbon dioxide and other acid forming substances which may be in the air and which may affect the indicator. The pretreatment of the air is not for purposes of getting pure air for the reaction in the sample tube, but rather to prevent foreign substances, particularly of an acid nature, from reacting with the indicator to be hereinafter referred to. The air moves from container **26** through the air inlet tube **28** which extends nearly to the bottom of the container **10** holding sample **12** being tested.

The pre-washed and dried air is caused to bubble vigorously through a measured sample of the oil **12** being tested. While heat from burner **20** raises the temperature of sample **12** at a controlled rate, the bubbled air along with vapors from sample **12** are conducted from container **10** through tube **30** into the container **32** which contains a measured quantity of a sensitive indicator. To aid in detecting the color change of the indicator, a small indirect light source may be used to illuminate it.

Tube **36** connects the stoppered container **32** to a suitable vacuum pump **38** which is used to draw the air through the system at a controlled rate. A manometer may be inserted at some convenient point in the train in order to maintain constant vacuum on the system during the period of testing. While a vacuum pump has been described in connection with the apparatus, it is possible to use a pressure pump at the other end of the system in order to force the air through the train.

The rate of heating of the sample **12** is very important, and it has been discovered that in order to obtain consistently accurate results the samples should be heated approximately 10° F. per minute. However, good results have been obtained when heat was applied at not less than 1° F. per minute nor more than 60° F. per minute. The temperature of the sample, as measured by the thermometer **14** inserted therein, at which the indicator **34** indicates acidity is defined as the acid vapor temperature of the sample.

In connection with the testing of substances other than lubricating oils such as semi-solid or solid substances, these may be placed in the container **10** in a partially crushed condition if desired and also, depending upon the nature of the substance, mixed with a suitable liquid of known properties. It is also desirable when working with certain materials to pre-heat the air prior to introducing it into the sample in the container **10**.

While the indicator **34** may be any of the known acid or alkaline indicators such as phenolphthalein, methyl red, and solid indicators, such as litmus, it has been discovered that much more accurate results are obtainable when an extremely sensitive indicator is used, such as a slightly alkaline alcoholic solution of methylene blue, which I have developed, and this indicator is preferred when hydrocarbons such as lubricating oils are being tested to determine their acid vapor temperature.

The methylene blue indicator, according to the present invention, is prepared as follows: To one liter of isopropyl alcohol, five to seven milliliters of a saturated solution of methylene blue in isopropyl alcohol is added along with approximately one milliliter of a saturated solution of potassium hydroxide in isopropyl alcohol. This mixture is allowed to stand for a period of approximately 24 hours, and after this period of standing should be of a red color. If, instead of red, the solution is found to be purple, a few additional drops of potassium hydroxide in isopropyl alcohol should be added. The indicator may then be checked for sensitivity by adding one drop of 0.1 N benzoic acid solution in isopropyl alcohol to ten milliliters of the indicator. If the indicator is of the proper degree of sensitivity, this should turn the solution definitely blue.

The total heating time for the sample being tested is also of importance in reaching accurate results, and it has been found that the total heating time of the sample should not be over ten minutes. As pointed out, the acid vapor temperature of oils ranges from approximately 330° F. for new oils to as low as 100° F. for severely deteriorated oils. The danger zone, that is, the point at which the oils become corrosive, occurs when the acid vapor temperature drops to 200 to 215° F.

When proceeding according to the present invention, it has been discovered to be essential to have the washing and drying containers **24** and **26** for the air which is to be bubbled through the samples. It has also been discovered that the ebullition of the air through the sample must be vigorous and that the air along with occluded vapors from the sample must also be brought into intimate and vigorous contact with a measured quantity of the indicator in the container **32**.

The following examples illustrate the manner of proceeding according to the present invention. These examples are illustrative only and the intention is not intended to be limited by the examples disclosed but only by the scope of the appended claims.

Example I

A measured sample of lubricating oil is placed in the container **10**. Vacuum pump **38** is activated and adjusted to draw a stream of pre-washed an dried air through tube **28** at a rate so that the air will bubble vigorously through the sample in the container **10**. The air and vapor from the sample being tested are conducted to a measured sample of methylene blue indicator in the container **32** so as to have vigorous and intimate contact with the indicator. Simultaneously with the movement of air through the system the sample of oil is heated approximately 10° F. per minute. As the temperature of the sample of oil rises, as indicated by the thermometer **14**, a continued observation of the methylene blue indicator is maintained, and the temperature of the sample at which the indicator first shows acidity indicates the temperature at which acid vapors may be expected to form from the oil in use.

Example II

The procedure for testing greases, highly viscous substances, pastes and semi-solids is as follows:

A measured sample of the substance is thoroughly mixed with a suitable solvent or thinner of known characteristics, and preferably one that is reasonably stable, and in such proportions as to render the mixture of the consistency of thin molasses. A measured sample of the mixture is placed in the container **10**. The procedure is then continued as for Example I.

In connection with the above example, greases thinned with fresh lubricating oil have shown acid vapor temperatures as low as 160° F. Used greases have shown much lower temperatures.

In the case of lubricating oils and greases the lowering of acid vapor temperature is a measure of the extent of

degeneration and an indication of incipient corrosion. These facts have been established by abundant experiments. In the case of paints, varnishes, molasses, foods, etc., the acid vapor temperature or the evolution of volatile acids could very well be a measure of their stability, rate of degeneration and other properties which would be valuable to determine storage characteristics.

Example III

Procedure for testing solid material.—Whenever practical the solid should first be crushed or pulverized by suitable means. A measured sample of the dry solid material is placed in container **10**. A filtering device such as a wad of surgical cotton is placed in container **10** a short distance below stopper **11** to prevent dust from the sample being carried over into the indicator **34**. Under extremely difficult conditions an additional container which serves as a trap to catch any dust which may pass through the filtering medium may be inserted in line **30** between container **10** and container **32**. The procedure is then continued as in Example I.

Example IV

A measured sample of the dry crushed or pulverized material or of wet crushed material, is suspended in a quantity of distilled water, or in a quantity of high boiling point liquid of known properties, and the suspension placed in container **10**. The procedure is then continued as in Example I.

In connection with running tests to determine the acid vapor temperature of solids, an extended investigation on soil corrosion has just been completed under my direction. In evaluating the soil to determine the constituents responsible for corrosion, volatile organic acids were suspected. The procedure of Example III and Example IV were applied. For the several soils tested acid vapor temperatures ranging from 170° F. to 215° F. were discovered which verified these suspicions.

Soils are rarely subjected to these temperatures. However, volatile organic acids will form more slowly under normal soil temperatures. These become serious corrosion hazards which may be especially severe where pipe lines are buried at shallow depths. An extreme example of this reaction may be illustrated in the case of a copper line buried about one foot underground in rich soil. The line completely disintegrated in about 14 months.

Example V

Effect of volatile vapors on metal.—The procedure is the same as for Example I, except that a sample of the metal to be tested is substituted for the indicator **34**.

Example VI

A cleaned strip of metal is placed in container **32** in place of the indicator, and the metal is partially submerged in distilled water. The pre-washed and dried air is vigorously bubbled through sample of substance in container **10**, then brought into intimate and vigorous contact with the distilled water and metal in container **32**. Simultaneously the sample **12** is heated at a specified temperature for a specified time. The metal is then removed from the distilled water, and the distilled water is checked for metal traces in solution or suspension by any of the known and published micro-chemical or colorimetric methods suitable for the particular metal.

Example VII

A cleaned strip of metal is placed in the dry container **32**. A second and similar container with a quantity of distilled water is inserted in line **36** and between container **32** and vacuum pump **38**. Prewashed and dried air is bubbled vigorously through the sample of substance in container **10**; the gas and vapors from sample **12** are passed through the dry container **32** containing the metal strip, and thence through the second container where said vapors are bubbled vigorously through the distilled water. Simultaneously sample **12** is heated at a constant specified temperature for a specified time. The distilled water is then checked for metal as in Example V.

The corrosive effect on metals of vapors from oils whose vapor temperature had been lowered by laboratory oxidation and from oils used in engines has been repeatedly demonstrated as per Examples V, VI and VII. Metal traces have been detected in the distilled water after as short a heating period as 15 minutes of an oil whose acid vapor temperature had dropped to 215° F. and which was heated during this test at 215°.

Positive corrosion results have also been obtained with solids such as the soils of Example III.

Example VIII

Procedure for testing gases.—A substance which is a gas or vapor at normal temperatures is drawn into the dry container **10** through a **T** in the inlet tube **28** at a specified rate and manner. With suitable adjusting valves, air may or may not, as the conditions require, be drawn in desired proportions through containers **24** and **26** and become mixed with the gas or vapor in tube **28** and container **10**. The air and gas or vapor mixture from container **10** are conducted to a measured sample of methylene blue indicator in container **32** so as to have vigorous and intimate contact with the indicator. Simultaneously with the movement of air and sample through the system the sample is heated approximately 10° F. per minute. As the temperature of the sample rises as indicated by thermometer **14**, a continued observation of the methylene blue indicator is maintained, and the temperature of the sample at which the indicator first shows acidity indicates the temperature at which acid vapors form and is a measure of the stability of the gas.

The feasibility of this procedure as applied to gases and vapors has been demonstrated in the case of gasoline vapors. The general procedure has been used except that the indicator has been replaced with a strip of metallic copper to determine the corrosive effect of the vapors directly.

I claim:

1. A process for determining the acid vapor formation characteristics of a substance selected from the group consisting of lubricating oils and greases and mixtures of the two, said substance having an acid vapor temperature not above about 160° F., which comprises the steps of applying heat at a continuously increasing temperature at a controlled rate to the sample to be tested and simultaneously with said application of heat passing a stream of pre-washed and dried gas vigorously through said sample, conducting the gas and vapors from said sample to a measured quantity of a volatile, acid-sensitive indicator and measuring the temperature of the sample at the precise time that said volatile, acid-sensitive indicator indicates the presence of acidic vapors in the gas and vapor products bubbling through said indicator, whereby from the temperature of said sample at which said indicator shows the first indication of acidity the acid vapor temperature of the sample may be ascertained.

2. A process as claimed in claim 1 wherein the rate of heating of said sample is 10° F. per minute.

3. A process as claimed in claim 1 wherein the rate of heating of said sample is within the range of 1° F. to 60° F. per minute.

4. A process as claimed in claim 1 wherein the bubbled gas and vapors from said sample are caused to have intimate and vigorous contact with said acid indicating medium.

5. A process as claimed in claim 1 wherein the gaseous substance comprises oxygen and mixtures thereof.

6. A process as claimed in claim 1 wherein the gaseous

substance is pre-heated to accelerate the breakdown of the test sample.

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