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INITIAL pH (i-PH) OF IN-SERVICE LUBRICANTS

MEASURING RISK POTENTIAL IN LUBRICANTS WITH ACIDIC COMPONENTS

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INTRODUCTION

Oxidative and thermal stress on a lubricant can produce many undesirable by-products that increase machine wear, and decrease tribological performance. Acids are some of the most impactful actors in the degradation of a lubricant, impacting the base oil and its additives. In oil and lubricant analysis, quantifying these acids can give insight into the net potential for oxidation and corrosion.

For most lubricant end users, the total acid number (AN), as described by popular standard methods (ASTM D664 / D974), is the most widely deployed measurement for this type of corrosion risk. The advantage of AN is that it is a quantification method that gives linear results that are intuitive to understand, and easily comparable to other AN values from other methods.

However, like most test methods, a single data point does not provide enough information for prescriptive or reactionary maintenance, especially when those decisions may incur significant monetary costs. Compounding this is that there are no set condemning limits for intervention because AN trends are variable between base stocks and additives, For example, AN does not discriminate between strong acids like hydrochloric (HCl), nitric (HNO3), or sulfuric (H2SO4) acids, and weak acids like carboxylic acids (RCOOH), or aryl-alchols (i.e., Phenol). This poses a secondary problem, as some of the weak acids (like Phenol) are intentionally placed additives to combat oxidative stress. Acid number, as the singular metric of corrosion potential, obviously does not paint the whole picture.

The most logical addition to the technicians' toolkit for layering on additional analyses measuring risk potential associated with acids, is measurement of the lubricant's pH. Measuring pH is a familiar procedure and metric for most technicians and analysts, even outside of scientific fields. The duality of acidity and alkalinity are ingrained as opposite ends of the pH spectrum, presenting seemingly binary information.

INTRODUCTION

Even so, the simplicity of pH as a measurement is deceptive, and requires thoughtful consideration. When used in tandem with other acid quantification metrics, it can provide a useful rubric for making intelligent and informed decisions surrounding your oil and lubricants.

Figure 1 shows how an operator can use the information provided by simultaneous i-pH/AN testing, and what actions that data indicates should be taken. This article will dissect the science behind this decision matrix, and why each quadrant indicates the quality and criteria shown.

Low i-pH / High AN

Risk Level: High

Corrosive Actors: Strong & Weak Acids (Nitric, Sulfuric, Organic)
Recommendation: Inspect components and change the oil; machine at high risk for acidic corrosion

High i-pH / High AN

Risk Level: Low to Moderate

Corrosive Actors: Weak organic acids
False Positive: Possible unnecessary lubricant changes or top-ups
Recommendation: Monitor i-pH for rapid decrease
Follow-up Action: Correlate i-pH with nitration and sulfation to determine strong acid onset

Low i-pH / Low AN

Risk Level: Low to Moderate

Corrosive Actors: Strong acids (Nitric, Sulfuric)
False Negative: Longer operating time under acidic conditions
Recommendation: Monitor AN for rapid increases
Follow-up Action: Determine if viscosity is on spec; monitor FTIR for oxidation and leading indicators of anti-oxidant depletion

High i-pH / Low AN

Risk Level: Low

Corrosive Actors: None or trace weak acid
Recommendation: If lubricant is within OEM specifications, follow machine performance with oil condition monitoring

Figure 1: Corrosion risk potential and recommended action based on i-pH/AN quadrants of results

What goes unsaid about pH, in most cases, is that it is only applicable to water based solutions. Thankfully there are methods that can determine the pH of dilute hydrocarbon mixtures, though because it is not measured in aqueous solvents, it is formally recognized as an ‘apparent pH’ – the pH that would otherwise be measured if the material was assumed to be water based. Terminology and usage of apparent-pH has shifted depending on the industrial application; in tribology applications and analyses, the term initial-pH is used synonymously.

While initial-pH, or i-pH, cannot be interpreted under the same rubric as standard pH, this does not indicate that it cannot be part of oil condition monitoring. When interpreted appropriately, it is a highly informative metric for determining corrosion potential. To validate its use in oil analysis, one must understand the foundations of the pH scale and its measurement. Below the reader will find the technical basis on which i-pH is considered a nuanced analytical technique, that can also bolster condition monitoring with a robust set of corrosion risk indicators.

TECHNICAL DISSECTION OF i-pH

The pH of a material has a nearly ubiquitous understanding and meaning to many scientific and industrial fields. It is understood that pH is a measure of ‘acidic strength’, that it has scale of dimensionless values from 0 (acidic) to 14 (basic), and that pH 7 means a substance is fully neutral; its calculation is similarly simplistic.

$$pH = -\log[\text{concentration of free hydrogen ions}] \qquad \text{(i)}$$

The true value of having such a simple metric by which to measure acidity is that it can seemingly translate comparatively between scientific disciplines, materials, and media. Treating pH as a transitive property of materials is safe in most real world applications.

It should be noted that pH is susceptible to significant fluctuation in the properties of the medium or solvent, such as conductivity, dielectric constant, hydrophilicity / hydrophobicity, and the unique chemical interactions of the medium with the material itself. Yet as mentioned earlier, pH is formally only a valid measurement for solutions where the solvent is predominantly water-based. Thankfully this does not exclude using pH to extract useful chemical insight from analyses on non-aqueous substances or matrices, though the interpretation of results must be scrutinized carefully.

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To begin understanding how pH is connected to i-pH, consider the rudimentary chemistry of acids and their pH. The informal definition of pH is simply ‘acid strength’. An acid’s strength is proportional to the amount of free and positively charged hydrogen (protons, written as H+) the acid can generate in solution. This is generally expressed by the following chemical equation:

$$HA \leftrightarrow H^{+} + A^{-} \qquad \text{(Eq. 1)}$$

In this reaction equation, the basic principle of acid dissociation is shown. Acids are neutrally charged molecules, with an abbreviated form ‘HA’, where ‘H’ is positively charged hydrogen, and ‘A’ is a negatively charged counter ion. In solution, some of this neutral acid will dissociate into protons (H+), and counter anions (A-). The two-way equilibrium arrow indicates this process can proceed in both directions, creating a potentially dynamic mixture of the acid and its dissociated components. Thus, an acid that significantly or predominantly dissociates towards the rights side of the equation is strong; examples of strong acids include hydrochloric (HCl), nitric (HNO3), and sulfuric (H2SO4) acids. An acid that only partially or incompletely dissociates is considered a weak acid; examples of weak acids include organic acids (RCOOH), and Phenols.

TECHNICAL DISSECTION OF i-pH

What Eq.1 fails to capture is that this dissociation is influenced by the medium in which HA is dissolved. Acids will interact with polar molecules of water, acting as a positive force for dissociation (Eq. 2).

However, if H2O is replaced with Benzene, the acid does not interact, with no stabilizing force to promote dissociation, so nothing will transpire (Eq.3).

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^{+}_{(aq)} + A^{-}_{(aq)} \qquad \text{(Eq. 2)}$$

$$HA_{(Bz)} + Benzene_{(l)} \rightarrow \text{No Reaction} \qquad \text{(Eq. 3)}$$

Even though in both Eq. 2 and 3 the same amount of acid (HA) is present, a pH cannot be measured in benzene due to the lack of protons formed. In Eq.2, water interacts with HA and associates itself with the proton, creating the hydronium ion (H3O+). However, if both solutions were titrated with a strong base, such as potassium hydroxide (KOH) as performed in AN analysis (D664), the same result would be returned. These two measurements appear to then contradict each other, except fundamentally AN and pH are measuring different properties of the chemical species in play. Total Acid Number quantifies the neutral acid molecule (HA), while pH quantifies the free protons (H+). From these two tests, one could then infer a qualitative picture of the chemical composition of any water-based solution. Refer to Figure 2 below for a succinct summary of this conclusion.

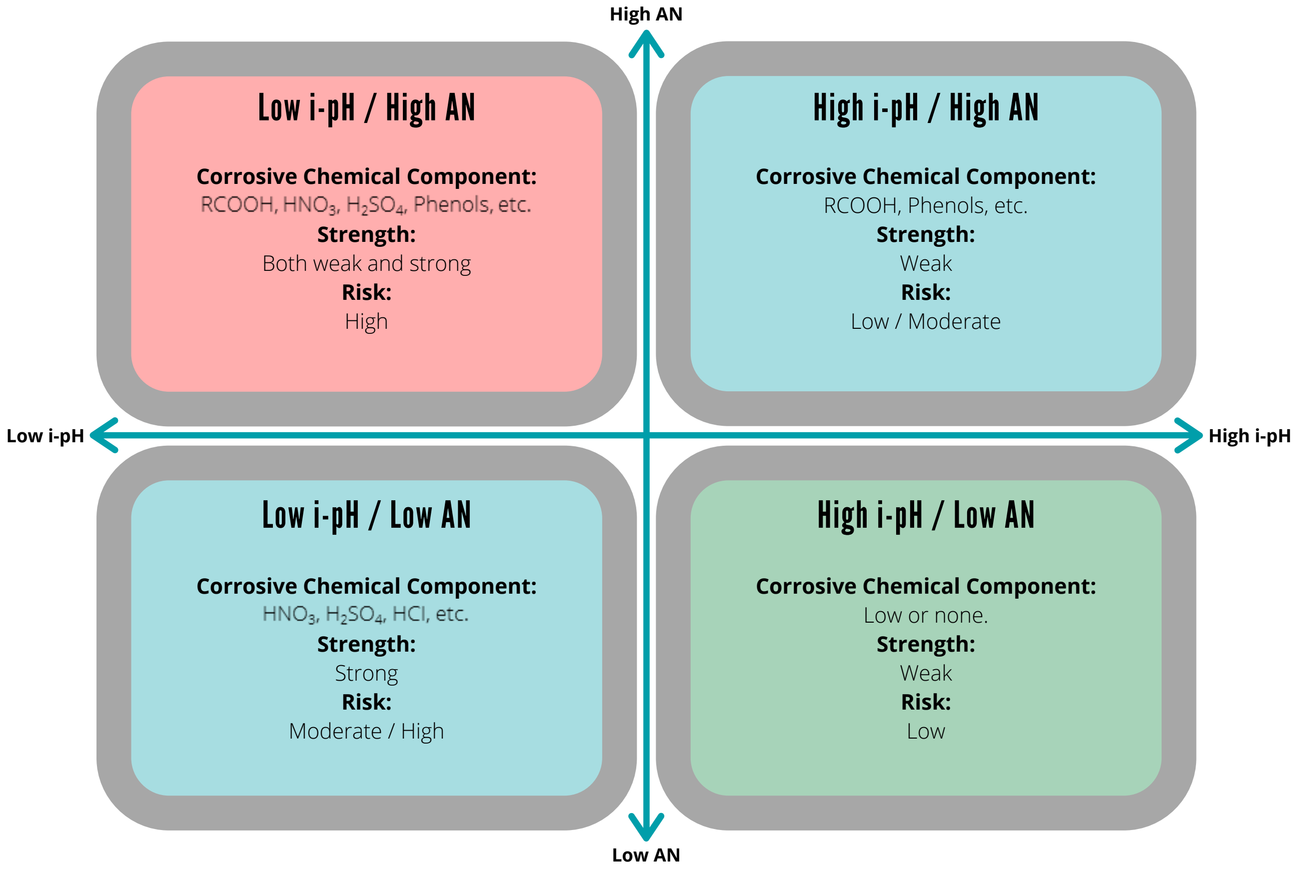

Figure 2: The four primary modalities of AN/pH results, interpreted as indications of corrosion risk based on the quantity and strength of the acidic components.

TECHNICAL DISSECTION OF i-pH

Compounding the barrier to utilizing pH in non-aqueous media: measurements, instrumentation and software are designed on the unified principle of detecting free protons in the hydronium form (H3O+). So, even if the generic HA molecule could dissociate in Benzene, the pH would remain unmeasurable by all conventional equipment. In reality, for many practical applications where the solvent medium is appreciably but not purely composed of water, the deviations that arise from non-aqueous components are acceptable for most use-cases.

But: 'What about solvent media wherein acids still dissociate, but where water conten is insignificant, or is an impurity, or is quantitatively zero?'. To answer this problem, consider the pH scale itself, and what it implies about the interpretation of the information it returns.

In the previous reaction equations, the solution media was water. Due to water being a polar and protic solvent (meaning it contains molecules that can potentially produce H+ when dissolved), it can undergo what is known as autoprotolyis; simply stated this means water can dissociate spontaneously when in liquid form, per Eq. 4.

$$H_2O \leftrightarrow H^+ + OH^- \quad \text{(Eq. 4)}$$

The degree to which autoprotolysis occurs is measured mathematically by a numerical 'dissociation constant', denoted by the letter Kw (the subscript 'w' indicates that the medium in question is water). This is calculated using the formula in Eq. 5, defined mathematically as the product of the concentration of both the free protons and hydroxide ions. In the case of water, the experimentally determined value of Kw is 10^-14. One can ascertain from Eq. 4, that in pure water there must always be a 1:1 ratio of protons and hydroxide ions after dissociation, thus their concentrations must be equal. With some simplification in Eq. 6, and using Formula 1 presented earlier, we can discover the pH for pure water.

$$K_w = [H_3O^+][OH^-] = 10^{-14} \qquad \text{(Eq. 5)}$$

$$K_w = [H^+][H^+] = [H^+]^2 = 10^{-14} \qquad \text{(Eq. 6)}$$

$$[H^+] = 10^{-7}\,;$$
$$\text{Thus pH} = -\log[H^+] = -\log[10^{-7}] = 7 \quad \text{(Eq. 7)}$$

The pH obtained for pure water is calculated as Eq. 7, exactly the intuitive result an experimentalist would expect to measure for water without any acids or bases present. Recall earlier that one of the generally ubiquitous facts about pH was that neutral mixtures have a pH of 7. An eagle-eyed technician will also notice that the exponent of Kw (in this case, -14) is similar to the maximum value of the pH scale itself (14). It can accurately be stated that for any solvent or media, the maximum pH will be the negative logarithm of the dissociation constant; though the scope of this paper does not necessitate the tedious mathematical exercise to prove such a thing.

TECHNICAL DISSECTION OF i-pH

This generalization allows for the measurement of pH in any medium where the solutes of interest can interact and exchange protons within the solvent; and wherein the associated instrumentation is compatible with the confluence of all substances present. For example, the auto-protolysis of methanol (CH3OH) is given in Eq. 8 with the associated constant of dissociation.

$$CH_3OH \leftrightarrow CH_3O^- + H^+ \,;\ K_{MeOH} = 3.2 \times 10^{-16} \quad \text{(Eq. 8)}$$

By the same deduction used for Eq. 5 – 7 above, the maximum pH for methanolic solutions is 15.5, and the neutralization point will correlate with a pH of 7.7. This is extendable to any generic solvent or solvent system (which can be abbreviated as SolvH; where the H represents a bound H+ ion, with the potential for dissociation from the solvent) as shown in Eq. 9.

$$SolvH \leftrightarrow Solv^- + H^+ \,;\ 0 < pH < -\log[K_{Solv}] \quad \text{(Eq. 9)}$$

While there is no sound way to compare measurements between disparately different solvent media, pH values will remain comparable within the same set of samples analysed with the same method and within the same solvent media. Additionally, the logarithmic scale remains intact, so a change of 1 pH unit corresponds to the same change in acid strength, irrespective of the medium.

Eq. 9 is then a powerful tool for justifying the use of pH in non-aqueous media, and for choosing the media in which to perform the analysis. If a solvent or solvent mixture is chosen such that K is effectively 0, like Benzene, Equation 9 returns an undefined result for the logarithmic calculation (commonly encountered as an error on the technician's calculator!). The power in Eq. 9 comes from recognizing that any solvent mixture with a non-zero K value, and any degree of polarity such that H+ might stably dissociate into the medium (like the base alcohols: ethanol and iso-propanol), a pH can be measured, and can return self-consistent results for the same solvent system.

It is at this point that the power and validity of i-pH is apparent. The ASTM method for determining the initial pH of petroleum products (D7946) prescribes a solvent mixture that is 50% toluene, 49.5% isopropanol, and 0.5% water – by virtue of having a polar component and water present, the K value will be non-zero. This solvent mixture is a long-standing recipe for what is colloquially known as 'ASTM medium', the standardized solvent mixture whereby miscibility of hydrocarbons and mineral oils, and polar or ionic substances is made possible by the significant proportions of toluene and iso-propanol respectively. A seemingly insignificant portion of water is added to provide the medium a route to form hydronium (H3O+) in the presence of acids; a requirement for conventional instrumentation to even measure a pH, as was discussed previously. ASTM medium also maintains adequate conductance and permittivity; properties that, while not necessary to dissect in this analysis, are critical for the function of all instrumentation for both AN and i-pH. All of these now rigorously justified properties mean any substance, as long as miscibility is possible in the ASTM medium, can have its apparent or initial pH measured accurately, with self-consistent results and interpretation.

TECHNICAL DISSECTION OF i-pH

Referring back to the modalities outlined in Figure 2 for the results of AN and i-pH, a similar model can be applied to lubricants and oils, shifting the interpretation of these results to reflect the industry specific applications and validating the use-case for i-pH.

Low i-pH / High AN

Intuitive & Expected: High AN equates to a lot of dissolved acid, typically correlated with a low pH value.
Chemical Presence: Both strong and weak acids
Diagnosis: High level of oxidation, leading to formation of strong (nitric, sulfuric) and weak (organic) acids.
Recommendation: Change the oil; component is at high risk for acidic corrosion.

High i-pH / High AN

False Positive: High AN equates to a lot of dissolved acid; however, high i-pH indicates the acids present are weak and present a low risk.
Chemical Presence: Weak organic acids
Diagnosis: AN on it's own may be causing oil changes more frequently than necessary, increasing costs.
Recommendation: Monitor i-pH for rapid decreases, indicating the onset of strong acid formation. If available, compare with nitration and sulfation levels to determine if oxidative stress is degrading the lubricant.

Low i-pH / Low AN

False Negative: Low AN indicates very small amount of acids present; however, i-pH indicates these acids are strong.
Chemical Presence: Nitric or Sulfuric acid
Diagnosis: AN on it's own misses this associated risk and may be causing longer operating time under higher risk conditions.
Recommendation: Perform secondary oxidation / nitration / sulfation tests to confirm presence of nitric / sulfuric acids. Perform oil change if out of spec, or monitor closely for increasing AN to indicate high risk operating conditions.

High i-pH / Low AN

Safe or Baseline: Low AN indicates very small or no acids present and i-pH supports this absence.
Chemical Presence: Nitric or Sulfuric acid
Diagnosis: AN on it's own misses this associated risk and may be causing longer operating time under higher risk conditions.
Recommendation: Perform secondary oxidation / nitration / sulfation tests to confirm presence of nitric / sulfuric acids. Perform oil change if out of spec, or monitor closely for increasing AN to indicate high risk operating conditions.

Figure 3: AN vs i-pH regime analysis and interpretations for in-service lubricants.

The significant conclusion from Figure 3 is that outside of the intuitive and expected results, there are two regimes where historically critical information was being missed, or potential for risk went undiagnosed. High AN results have been grouped together as having a high corrosion risk, due to the indiscriminate nature of the test method. Yet when AN and i-pH are concurrently high, it can be inferred that while the absolute concentration of acidic components is high, the acids present are weak and of low risk (an operator might be changing their oil prematurely if this AN result is taken at face value). In regimes where AN returns a low result, there would have traditionally been no flagged corrosion potential. Yet as was discussed previously, a low concentration of strong acids can still yield a low pH value, indicating the present risk of corrosion. Without i-pH, this corrosion potential would go completely unnoticed, preventing the operator from making informed and timely decisions surrounding the drain interval of their equipment. In the absence of i-pH to properly categorize this corrosion potential, an operator might have missed the point at which their lubricants were compromised, leading to increased wear on the machine.

SUMMARY

The information obtained from interpreting AN and i-pH taken together as a dynamic metric provides manifold insight into the chemical nature, reactivity, and composition of in-service lubricants, which can highlight complex flags for other sources of degradation. Historically acid number was measured in tandem with base number in the hope of catching a high trending acid number concurrent with a low trending base number; however in circumstances where neither of these measurements yields obvious results, the result loses value. Initial pH solves this by generating meaningful chemical insight when data points don't fall into prescribed or obvious patterns.

It is for this reason that i-pH is considered a necessary and integral part of condition monitoring. If oxidation, corrosion, thermal stress, and varnish are of concern in your machines and systems, then simultaneous measurement of AN and i-pH will provide the information necessary to extend drain intervals and locate premature failure of lubricants leading to corrosion.

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