DEVELOPMENT OF A NEW ASTM METHOD USING MEMBRANE PATCH COLORIMETRY

Varnish is often considered a transparent or translucent coating applied to various surfaces to provide a protective and decorative finish. However, in the petroleum industry, varnish has a very different meaning compared to machinery. Varnish, in this context, is defined as an insoluble film deposit that forms on surfaces [3]. This insoluble film can often cause detrimental damage to machinery [3].

Varnish is formed through a complex process involving the degradation and oxidation of lubricating oils in machinery and can cause detrimental damage to machinery, such as reduced oil flow, sluggish operation, loss of system control, bearing deposits, and pump failure [9]. Lubricating oils exposed to high temperatures, pressure, and other operating conditions undergo chemical changes that can form varnish due to the degradation of its physical and chemical properties. Varnish thereby forms on surfaces inside turbine lubrication systems such as pipes, tanks, bearings, heat exchangers, and servo-valves [4]. With the presence of varnish in machinery, companies may experience increased maintenance costs, unplanned downtime, and reduced equipment lifespan. By implementing varnish condition monitoring programs, such as the use of Standardized Testing and Enhanced MPC Methods, organizations can detect and mitigate varnish-related issues at an early stage, leading to improved equipment reliability, optimized maintenance schedules, and enhanced operational efficiency [7].

Several factors influence the formation of varnish. According to the National Library of Medicine, high temperatures accelerate the oxidation process and expedite the breakdown of the oil, leading to faster varnish formation [1]. Contaminants, such as water, solid particles, or degraded additives, can also contribute to varnish formation by acting as catalysts or providing reactive sites for chemical reactions. Improper synthesis of oils is another source of varnish, as improper oils react with lubricating oils to produce precipitates [1]. Further examples can be seen in Figure 1 on lesser-known factors.

The most common mechanism behind varnish formation is oil degradation caused by oxidation. As the oil degrades, various byproducts are formed, including polar compounds, acids, sludge, and insoluble particles. These byproducts can combine and undergo chemical reactions to form varnish-like substances, which can vary depending on factors such as the type of oil, operating conditions, and the presence of additives or contaminants. As varnish is typically a complex mixture of oxidized oil components, resins, polymers, and other insoluble materials, varnish can range in color depending on the severity of the degradation process. Varnish formation is a gradual process that occurs over time as the oil undergoes continuous degradation in service. If not addressed, this degradation can lead to reduced lubrication efficiency, increased friction, restricted flow, and potential equipment failure. To mitigate varnish formation and its detrimental effects, various strategies are employed. These include the use of high-quality lubricating oils with improved oxidation stability, proper filtration and maintenance practices, and the implementation of varnish condition monitoring techniques such as colorimetric patch analyzer method and membrane patch colorimetry test. By monitoring varnish levels and taking proactive measures, such as oil filtration, fluid replacement, or equipment cleaning, operators can minimize varnish formation and maintain the performance and longevity of machinery.

Even with the previously stated mitigation techniques being used, Exxon Mobil has reported that approximately 40% of the 192 power plants were reported to experience varnish-related problems [2]. Furthermore, according to Chevron Lubricants downtime and repair costs caused by varnish can run from $100,000 to the millions [6]. As a result, researchers and industry professionals have dedicated efforts to develop further and refine varnish condition monitoring techniques to safeguard the performance and longevity of equipment. Cases of this can be seen in ASTM D7843, which provides a standardized approach for quantifying insoluble color bodies in turbine oils. This quantity can serve as an indication of varnish formation.

ASTM D7843 involves filtering a representative oil sample through a membrane patch and evaluating the color intensity of the retained insoluble particles [5]. The determined color intensity is then compared to a standard color chart to evaluate the varnish level. This test method enables operators to monitor varnish formation in turbine oils and assess the potential for detrimental effects on equipment by employing membrane patch colorimetry. It provides a quantitative measurement that can be used for trend analysis and comparison against established thresholds or industry guidelines. Developing and utilizing such standardized test methods demonstrate the industry's commitment to monitor and manage varnish-related issues effectively. Thus, by implementing these techniques, operators can identify varnish formation early on and take appropriate actions, such as fluid filtration or replacement, to prevent further accumulation and mitigate potential damage to machinery.

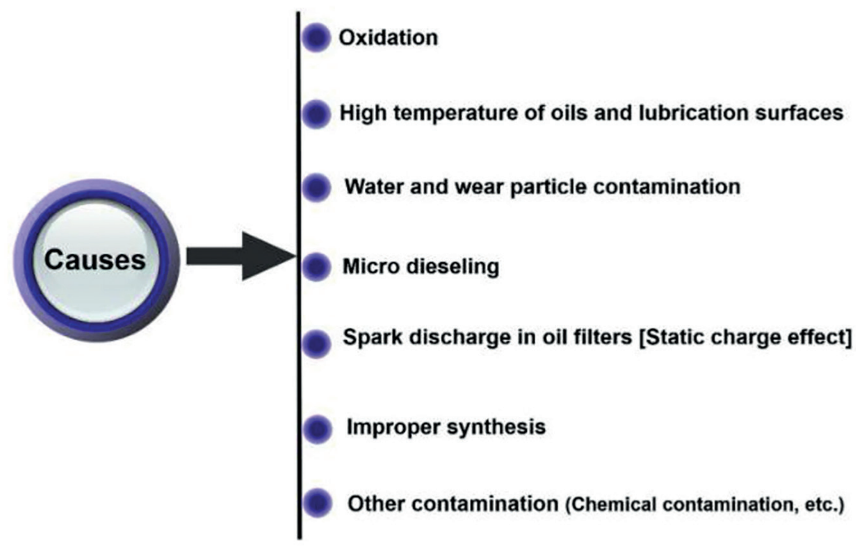

Figure 1: Causes of Varnish

While ASTM D7843 specifically focuses on Insoluble Varnish (I-MPC), many researchers are investigating soluble varnish (S-MPC). Insoluble varnish is typically the primary concern in machinery, however, soluble varnish can also have detrimental effects on equipment performance and reliability. Soluble varnish refers to a type of varnish that remains suspended in the oil and does not form deposits within the system. Insoluble varnish occurs when the oil becomes overly saturated with soluble varnish. This causes it to begin to plate out and adheres to the surfaces of the system, which leads to hot spots, micro-dieseling, and wear. [7]. Researchers actively study soluble varnish and its implications in industrial settings. This research involves understanding soluble varnish's formation, composition, behavior, and potential applications. Researchers investigate soluble varnish to uncover new insights and strategies to manage varnish-related issues in machinery effectively. It is important to note that soluble varnish is not applicable for formulations that are dyed, and colloidal carbon can also influence test results. Soluble varnish should be monitored along with Insoluble varnish considering L*a*b* values and their correlations.

In a study conducted by Wasan Chokelarb and his team, Chokelarb investigated the significance of both soluble and insoluble varnish test methods in monitoring varnish buildup in mineral turbine oil. Chokelarb believed that the use of only insoluble varnish data would be insufficient and may cause inaccurate and ineffective maintenance decisions. Thus, ASTM D7843 was modified to work with soluble MPC along with the insoluble outlined in the original ASTM D7843.

The study used the in-service turbine oil samples of three different power plants to perform the previously mentioned ASTM D7843 as well as the modified method. Condense The first oil sample was analyzed every two months within a period of two years. As seen in Table 1, the sample results caused the team to conclude that ASTM D4373 is not applicable to all oil types and equipment combinations, for Sample One shows that the turbines from which the oil was taken were already experiencing an accumulation problem. Therefore, even if the amount of MPC did not reach the limit, the turbine is currently experiencing issues with accumulation. This was unaccounted for in the ASTM method. Thus, the consensus made from the results is that the ASTM limits should be used only as a general guideline, and that in the future the use of oil analysis results along with physical examination of the equipment should be used to set a limit specified for each oil and equipment combination. The results of the sample turbine can be seen in Table 1.

Sample Two of this study was used to monitor quality and varnish build-up. This sample used a VRT, or depth media filter, to clean the oil system. This method of monitoring and controlling varnish buildup resulted in the cleansing of large amounts of insoluble varnish from the system, allowing it to go below the threshold of ΔE 30. While the insoluble varnish levels were reduced, the levels of soluble varnish were not addressed and increased over the course of the study. Chokelarb and his team suggested that the use of electrostatic filters could be a possible

Table 1: Oil Analysis for Plant #1 Turbine

Sequence #	Limits	Reference	1	2	3	4	5	6
Date Sampled		New Oil	2019/5/30	2019/6/27	2019/8/30	2019/10/31	2020/1/30	2020/5/28
Oil Hours		0	22	693	1802	3236	5121	6502
Turbine Hours		-	22908	23579	24688	26122	28007	29391
Viscosity @40 C, cSt	30.6-33.9	32.3	32.6	32.4	32.7	32.7	32.3	32.7
Water Content (%Wt)	<0.02	0.012	0.016	0.029	0.016	0.023	0.024	0.013
Total Acid Number (mg-KOH/g)	<0.17	0.07	0.059	0.055	0.075	0.083	0.163	0.175
% Aminic AO Remaining	>25	100	99	92.5	90.3	89.8	87.7	78.4
Particle Count > 4 µm	<1300	656	2631	2463	6260	3608	6009	190511
Particle Count > 6 µm	<320	80	193	121	1070	565	669	12659
Particle Count > 14 µm	<40	8	11	8	24	63	46	2969
Oxidation (abs by FTIR)	<10.5	7	7.8	8.1	8.9	9.5	13.7	13.8
Solube-MPC (ΔE)	<30	2.4	3.7	6.2	6.2	6.7	10.6	16.3
Insoluble-MPC (ΔE)	<30	1.6	2.3	11.1	10.4	15.7	23.8	24.6
Sludge Weight (mg/100ml)	<10	0.8	3	3.3	3.6	4.4	5.9	7.6

Table 2: Oil Analysis for Plant #2 Turbine

Sequence #	Limits	Reference	1	2	3	4	5	6	7
Date Sampled		New Oil	2019/7/3	2020/3/11	2020/6/18	2020/12/23	2021/3/29	2021/6/25	2021/10/18
Oil Hours		0	7749	13308	15398	19447	21514	23368	25948
Turbine Hours		0	7749	13308	15398	19447	21514	23368	25948
Viscosity @40 C, cSt	41.1-45.6	43.4	42.9	43.1	43	43.4	43.2	43.2	43.1
Water Content (%Wt)	<0.02	0.012	0.017	0.018	0.017	0.012	0.021	0.022	0.011
Total Acid Number (mg-KOH/g)	<0.17	0.07	0.044	0.063	0.088	0.141	0.137	0.135	0.105
% Phenolic AO Remaining	>25	100	99	98.4	94.3	93.6	93.1	89.1	87.5
% Aminic AO Remaining	>25	100	60.7	51.6	31.4	37.8	28.4	19.5	14.2
RPVOT (%Oxidation Stability Remaining)	>25	100	90	-	87	85	-	83	-
Particle Count > 4 µm	<1300	305	15029	6869	17525	16917	28194	31808	328
Particle Count > 6 µm	<320	82	7373	5233	3388	2754	21979	9156	88
Particle Count > 14 µm	<40	25	1403	1433	1456	186	2369	20	13
Oxidation (abs by FTIR)	<19.5	13	14.8	15.4	16.9	15.4	16.1	15.2	14.9
Solube-MPC (ΔE)	<30	1.2	24.8	27.7	34.5	44.1	38.8	24.5	41.7
Insoluble-MPC (ΔE)	<30	1.5	5.8	9.4	32.4	31.4	50	57.8	2.6
Sludge Weight (mg/100ml)	<10	1	1.3	3.8	4.4	7.9	12.1	22.2	1.6

Table 3: Oil Analysis for Plant #3 Turbine

Sequence #	Limits	Reference	1	2	3	4	5	6	7
Date Sampled		New Oil	2017/11/22	2019/2/27	2019/9/9	2020/2/14	2020/3/27	2020/4/28	2020/6/31
Oil Hours		0	4320	15120	20976	22992	23952	27168	28488
Turbine Hours		-	153624	164424	170280	173256	174240	176472	177792
Viscosity @40 C, cSt	29.6-32.7	31.2	31.4	31.8	32.1	32.1	32	32	32.2
Water Content (%Wt)	<0.02	0.01	0.01	0.02	0.02	0.03	0.02	0.02	0.01
Total Acid Number (mg-KOH/g)	<0.4	0.15	0.2	0.13	0.23	0.18	0.18	0.12	0.11
% Phenolic AO Remaining	>25	100	80.4	78.7	70.7	66.2	62.4	57.3	56.9
% Aminic AO Remaining	>25	n/p	n/p	n/p	n/p	n/p	n/p	n/p	n/p
Particle Count > 4 µm	<1300	355	811	8243	30645	28253	21244	318	238
Particle Count > 6 µm	<320	71	102	97	713	900	15279	86	50
Particle Count > 14 µm	<40	8	13	14	17	15	79	12	4
Oxidation (abs by FTIR)	<19.5	8.6	9.2	9.7	10	10.6	10.7	10.2	10.6
Solube-MPC (ΔE)	<30	2.1	17.4	30.7	31.3	33.7	35.8	37.8	39.5
Insoluble-MPC (ΔE)	<30	1.5	16.9	41.4	68.3	69.9	75.4	12.1	12
Sludge Weight (mg/100ml)	<10	1.5	3	3.2	3.8	4.3	5	1.5	1.6

solution to this issue and will reduce soluble varnish levels in the system. Additionally, it was concluded that the phenolic antioxidant.

levels for this sample dropped to critical levels due to the presence of varnish. This observation implies that the oil has reached the varnish saturation point [8]. Results of this sample can be seen in Table 2: Oil Analysis for Plant #2 Turbine Oil

Sample Three was collected from Small Power Producers (SPPs) power plant, which are private or state enterprise that generates electricity either (a)

non-conventional sources such as wind, solar and mini-hydro energy, or fuels such as waste, residues, or biomass. This power plant experienced an overheating issue in the turbine system. As a result, insoluble black particles were suspended and produced. These particles are carbonized products caused by thermal degradation [8]. However, this was not necessarily varnish because these particles might have been caused by the process of coking, which is the heating of coal in the absence of oxygen to a temperature above 600 °C to drive off the volatile components of the raw coal, leaving a hard, strong, porous material of high carbon content called coke. Results of this sample tested via ASTM D7843 showed that there was a reading as high as 75.4, which is more than twice that of the limit of 30, of insoluble varnish. Carbonized results are not accurate, as the carbonized products influenced the result of this method. The modified ASTM D7843 experienced better results, for it enabled the differentiation between IMPC and the coke, providing a better reading of the sample. The powerplant used off-line filtration to clean the black particles. This system reduced the amount of insoluble varnish. However, the soluble varnish levels remained the same. This led to the conclusion that the sample oil reached its saturation point and over time, insoluble varnish might stick out again on the surfaces [8].

Data regarding this sample can be seen in Table 3.

The end results of the study conclude that the synergistic effect of testing both soluble and insoluble MPC helps in giving more effective and accurate information that influences decisions for maintenance and upkeep. Also, this study gives insight into the root causes of varnish and the justification behind the cause [5]. Furthermore, the appropriate varnish removal technology can also be applied depending on the results of both soluble and insoluble MPC. Therefore, soluble MPC is also another major consideration that the industry must investigate otherwise, it may lead to potential disasters.

Ultimately, varnish control monitoring should be a priority for all companies as the effects of both insoluble and soluble varnish can have detrimental effects on machinery. Furthermore, companies should ensure that their focus does not remain solely on insoluble MPC but also on soluble MPC. If not, the costs of maintenance may drastically increase as the soluble MPC can cause damage to entire lubrication systems, causing more need for maintenance.

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