

WHITE PAPER

New Approach for Controlling Varnish in Lube and Hydraulic Systems

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BACKGROUND

There is a plethora of varnish mitigation technologies available for mitigating varnish in large-volume lube oil sumps. These technologies are commonly installed on turbine oil reservoirs. However, there are so many other applications where varnish and deposits create reliability concerns, such as hydraulic units, gearboxes, and compressors. Even wind turbines can have performance problems due to deposit formations.

Many of these applications have too small of a reservoir to justify installing a varnish mitigation system. Some of these formulations also have additive components that can be removed by several of the varnish mitigation technologies. The presentation illustrates a novel approach to control deposits in these applications and presents several case studies illustrating the benefits of eliminating varnish in these applications such as compressor, pulverizer, wind turbines, and tube drawing applications.

WHAT DO WE MEAN BY VARNISH?

The nomenclature of oil-derived deposits is expansive. Names such as sludge, lacquer, goo, gunk, oil slime and many others are often used to describe deposits found inside lubricated machines. Varnish is the most common phrase used to refer to oil-derived deposits. Sometimes, sludge is differentiated from varnish as being a deposit that is wipeable compared to a more tenacious film thought to be varnish. From a chemical perspective however, there are dozens of different chemistries that make up oil-derived deposits, based on the operating conditions of the machine, formulation of the oil and contaminants that influence oil degradation pathways.

There are numerous resources available to understand the formation of deposits and how to chemically characterize them based on its mode of degradation. For this paper, we characterize oil-derived deposits as either soluble or insoluble, as this is the most significant characteristic of the deposit to understand mitigation strategies.

Solubility is defined by how much solute can dissolve into a solvent to make a homogeneous solution, as seen in Fig 1. An oil's solubility in the context of this paper is how much varnish it can dissolve.

Soluble deposits are those that can be dissolved into the lubricant matrix. Most oxidation by-products and turbine oil deposits are soluble. They can transition in and out of solution based on the equilibrium between the solute (varnish) and the lubricant

formulation (solvent). Although the lubricant formulation plays a role in its solubility, temperature and molecular size of the degradation products are the two most significant factors. The warmer the fluid, the higher the solubility of the deposits in the fluid.

Insoluble deposits are those that cannot be dissolved into the lubricant matrix, regardless of its solubility. Dirt is an example of an insoluble contaminant. Regardless of whether the fluid is formulated with a Group I or Group II base stock or whether the oil is at operating or room temperature, dirt is not going to dissolve into it. Examples of insoluble varnishes include depleted organometallic additives and coke deposits formed due to extreme thermal stress.

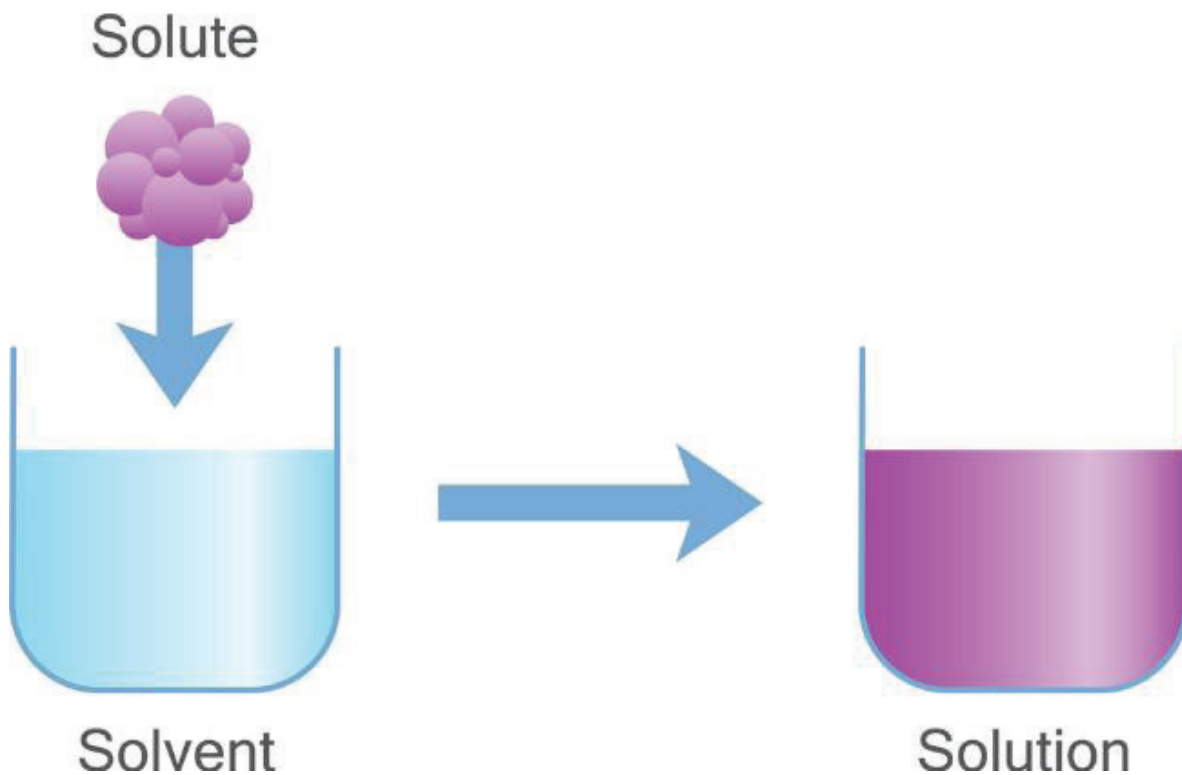


Figure 1: Solubility is defined by how much solute can be dissolved into a solvent and is an essential characteristic for understanding lube oil deposits.

Ashless formulations like turbine and compressor oils, that degrade primarily due to oxidation, create soluble varnish. ZDDP-containing hydraulic oils can form insoluble varnish consisting of sulfates and phosphates.

However, even in these formulations, varnish is comprised of both soluble and insoluble materials. This was first identified by A. Sasaki and referred to as “the sandpaper effect”, as can be seen in **Fig. 2**.

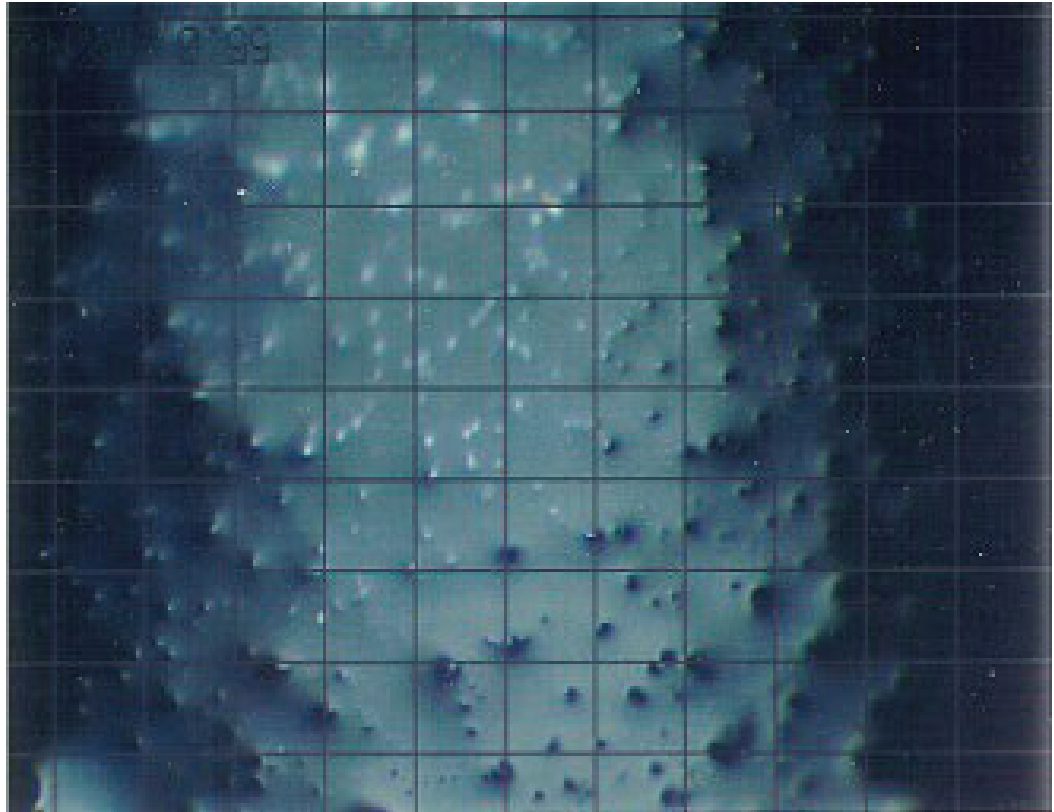


Figure 2: Microscopic image of a varnished “sandpaper” surface comprising of both soluble and insoluble deposits. Source: A. Sasaki.

THE DELETERIOUS EFFECTS OF VARNISH

Over the last 20-years, varnish has been a high-profile issue in turbines due to the expensive reliability issues. The power generation industry has become acutely aware of varnish, how to predict its formation through oil analysis tests such as the MPC test (ASTM D7348)¹ and what varnish mitigation strategies are effective. Turbine oils have also evolved to provide much stronger deposit control performance than previous generation turbine oil formulations.

Unfortunately, other industries are behind power generation when it comes to understanding varnish and its impact on reliability. Partly due to the operational impact that varnish has in other applications. Varnish in a large frame gas turbine that causes a unit trip can be an operational event causing >\$100k to a plant's bottom line.

Similar varnish in a plastic injection molding machine, however, may cause operational decay that can be partially overcome by tweaking machine controls. The result may be a decline in production yield. Although this is a far less dramatic event as compared to unit trip at a power plant, the cost may be higher when extrapolated over a year's worth of production multiplied by the number of machines in operation.

The formation of varnish creates the following changes in operational parameters:

- Reduced oil flow paths
- Sticking of moving parts
- Seal deterioration causing leaks
- Insulation effect impairing the oil's ability to act as a coolant causing components to be hotter and energy costs to increase, low thermal conductivity and low heat capacity
- Increased wear rates
- Plugging of filters and coating of sight glasses
- Reduced life of the oil as oil degradation products are catalysts that consume antioxidants

The ramification of these operational changes is manifested differently depending upon the application.

Here are a few examples of the deleterious effects of varnish in non-turbine applications:

- **Plastic Injection Molding Machines** may experience slower clamp speed or cycle time impacting production yield
- **Paper Machines** may have reduced precision in their rolls impacting the quality of their product
- **Air Compressors** may experience vibration in their bearings
- **Refrigeration Compressors** may have deposit formation impacting the sealing between low and high pressure
- **Gas Compressors** may experience high bearing temperatures

- **Hydraulic Presses** may experience stick-slip phenomena, impacting part quality
- **Plywood Presses** are at risk for valve failure resulting in the press being stuck together with strong adhesive
- Industrial Gearboxes may experience accelerated gear wear due to the sandpaper effect of varnish
- **Hydraulic Elevators** may experience chattering and sudden starts/stops due to deposit formation
- **Pulverizers** may experience high operating temperatures and increased filter clogging
- **Hydraulic Drawbench** may experience severe seal leaks and high temperature severely deteriorating the tube quality

Regardless of the applications, varnish deposits increase maintenance costs during turnarounds, requiring extra resources to decontaminate and flush the lube systems. If lube oil systems are not properly decontaminated between oil changes, one can expect the new charge of oil to last about half as long due to the catalytic effects of residual varnish in the system.

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- 1 ASTM D7843 - 18 Standard Test Method for Measurement of Lubricant Generated Insoluble Color Bodies in In-Service Turbine Oils using Membrane Patch Colorimetry
 - 2 Increasing Varnish Mitigation Performance by Incorporating Customizable ESP Media

WHY TRADITIONAL VARNISH MITIGATION TECHNOLOGIES MAY NOT WORK IN ALL APPLICATIONS

Current varnish mitigation technologies are delivered in the form of low-flow, kidney-loop filter systems designed to remove oil degradation products.

The commonly used technologies to mitigate varnish include:

- **Ion exchange resins** – the technology of choice for removing soluble oil degradation products at operating temperature;
- **Depth media filter systems** – the technology of choice for removing soluble oil degradation products at room temperature;
- **Electrostatic oil cleaning** – the technology of choice for removing insoluble oil degradation products.

Although these technologies are all effective when deployed in the right application, the justification for using these technologies in non-turbine oil applications becomes questionable from both a technical and economic perspective.

Varnish mitigation technologies can remove some oil additives when used in non-turbine applications. For example, resins can remove some additive chemistries, such as some ZDDP antiwear agents. Electrostatics and depth media filters can remove foam inhibitors, especially siloxanes, which are commonly used in gear oil applications.

The economic viability of installing a varnish mitigation system also becomes questionable on non-turbine oil systems due to lower reservoir volume. Below is the relative cost of installing a varnish mitigation system based on reservoir volumes:

Table 1: Relative cost of installing a varnish mitigation system based on reservoir volume.

Reservoir Volume (gals)	Capital cost (\$)	Cost/Volume (\$/gal)
3000	18,000	6
1000	18,000	18
500	18,000	36
100	18,000	180
50	18,000	360
10	18,000	1800

ANOTHER VARNISH MITIGATION SOLUTION IS NEEDED

For both technical and economic reasons, an alternative solution for varnish is necessary for these non-turbine applications. The authors investigated the use of Solubility Enhancing agents as a deposit control solution for non-turbine applications, as this addresses scalability, normalizing the cost of a varnish solution regardless of reservoir volume.

For a Solubility Enhancer to be a viable technical solution, it must meet the following conditions:

1. Miscible in the lubricant, allowing it to be added to an in-service lubricant during machine operation without the use of specialized blending equipment.

2. Wide range of compatibility both with in-service oils and system materials, such as seals and paints.
3. No impact on in-service oil's ability to interact with contaminants, such as air and water. Tests such as air release, foam and demulsibility cannot be adversely impacted.
4. No surface-active ingredients which could potentially interfere with an oil's corrosion inhibitors, antiwear, extreme pressure or friction modifier additive systems.
5. Engineered to effectively solubilize oil degradation products with an ability to hold a very high amount of varnish precursors without concern of them dropping out under oxidative stress.
6. Ability to effectively work without a varnish mitigation technology installed.
7. Ashless technology that doesn't contribute to varnish formation even under extreme oxidative conditions in the absence of antioxidants.

As part of this research initiative, over 20 Solubility Enhancing technologies were studied and a solubility parameter tool was developed which enable the creation of **Solvancer™**, a novel chemistry that meets the above technical criteria and provides a highly effective technology to solve varnish problems in non-turbine applications.

SOLVANCER: A NOVEL TECHNOLOGY AT IMPROVING DEPOSIT CONTROL AND MITIGATING VARNISH

Solvancer is a blend of specialized synthetic API Group V chemistries. The technology has outstanding solubility characteristics. It is also compatible with a wide range of base oils and fully formulated lubricants. Solvancer doesn't impact system materials such as seals, filters or paint. It has excellent oxidation stability and long-term deposit control characteristics. Solvancer does not cause any adverse impact on fluid properties and does not use surface-active chemistry.

Hansen Solubility Principles

One of the fundamental principles of solubility is that *like dissolves like*³. Oil degradation products are more polar than the non-polar state of the lubricant that derived them. Aniline point (ASTM D611)⁴ is often used to determine the polarity of a lubricant and to suggest its solubility. In reality, understanding lubricant solubility is much more complicated. In order to create a more realistic solubility model to determine varnish solubility, we used the Hansen Solubility Parameters. This model was originally developed to predict the solubility of polymers in solvents and lends itself very well to this application. Varnish compounds have similar solubility parameters as Solvancer.

3 Hansen Solubility Parameters: A User's Handbook, Second Edition, By Charles M. Hansen

4 ASTM D611 Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents

The three parameters used in this model are polarity (δ_p), hydrogen bonding (δ_h), and dispersive forces (δ_d)⁵⁶. These parameters make up the 3-dimensional axes in the Hansen Sphere. The effectiveness of the Solubility Enhancer is defined by a sphere with a radius that encompasses oil degradation products. If the properties of the varnish-causing contaminants reside inside this sphere, they will dissolve effectively.

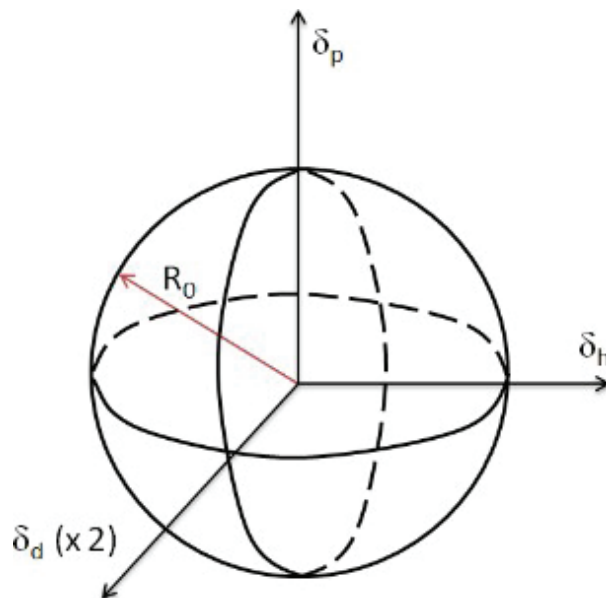


Figure 3: The three Hansen Parameters make up a sphere referred to as Hansen space and can be a useful tool for understanding varnish solution in a lubricant.

Performance Testing of Solvancer

Compatibility testing is the first step to ensure no adverse effects are seen when Solvancer is used in various lubricant formulations. Compatibility testing was performed according to ASTM D7155 at the maximum suggested treat rate for Solvancer (5%), the results of which can be seen in [Table 2](#).

Table 2: Results of Solvancer Compatibility Testing with various oil formulations.

OIL MIXED WITH 5% SOLVANCER™	D7155; PASS/FAIL
API GROUP I	Pass
API GROUP II	Pass
API GROUP III	Pass
API GROUP IV	Pass
Turbine Oil 1	Pass
Turbine Oil 2	Pass
Turbine Oil 3	Pass
Turbine Oil 4	Pass
Hydraulic Oil (ZDDP)	Pass
Hydraulic Oil (Ashless)	Pass
Compressor Oil	Pass
Synthetic Gear Oil	Pass
Mineral Gear Oil	Pass
Paper Machine Oil	Pass
Wind Turbine Oil 1	Pass
Wind Turbine Oil 2	Pass
Refrigeration Oil	Pass

5 ASTM D1331 Standard Test Methods for Surface and Interfacial Tension of Solutions of Paints, Solvents, Solutions of Surface-Active Agents, and Related Materials

6 ASTM D971 Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method

A simple way to determine how a Solubility Enhancer impacts a fluid's varnish potential is by performing before and after MPC tests. In these experiments, the Solubility Enhancer is added to the fluid at room temperature and then agitated for 24-hours. The oil treatment works rapidly at operating temperature improving the key uptime parameters within 24 hours of operation in most of the cases.

The effect of Solvancer to a fluid's MPC tests are immediate, as shown by images of the patches below:

Figure 4: MPC results of 5% Solvancer in a PAO-based Compressor Oil, which lowered the MPC from 48 to 6.



Figure 5: Impact of Solvancer on a Group II-based Air Compressor Lubricant, which lowered the varnish potential from 67 to 11. One can observe that the constituency of the deposits on this patch appear different than in Fig. 4.



In addition to short-term tests on the Solubility Enhancer's effect on varnish potential, accelerated oxidation tests are also of value. We conducted a Turbine Oil Performance Prediction Test (TOPP), according to ASTM WK688867, on new oil and compared the results to the new oil with Solvancer stressed for 6 weeks under the same conditions. The results of oxidation tests can be seen in Table 3.

Table 3: Results of New Oil and New Oil + Solvancer after 6-weeks of oxidative stress in the TOPP test.


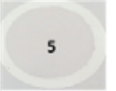
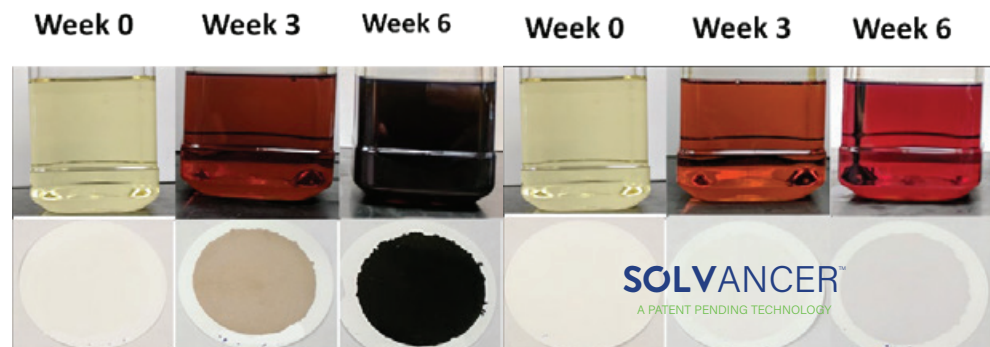
	New Oil	New Oil Stressed for 6 weeks	New Oil + Solvancer Stressed for 6 weeks
Ruler, ASTM D6971			
Area Aminic (% vs. New Fluid Standard):	100%	50%	52%
Area Phenolic (% vs. New Fluid Standard):	100%	19%	27%
Membrane Patch Colorimetry, ASTM D7843 ΔE	5		
Demulsibility @ 54°C, ASTM D1401 Oil-Water-Emulsion/Minutes	40-40-0/10	40-40-0/10	40-40-0/10
Foaming Characteristics, ASTM D892			
Sequence I, ml foam/seconds to break	20/0-4	20/0-4	0/0-0
Viscosity, ASTM D445			
100°C Viscosity, cSt	5.5	5.6	5.6
40°C Viscosity, cSt	32.7	32.7	33.1
Viscosity Index	106	106	106
TAN, ASTM D664, mg/KOH	0.15	0.05	0.05
RPVOT, ASTM D2272, minutes	1222	302	355

Table 3: Results of New Oil and New Oil + Solvancer after 6-weeks of oxidative stress in the TOPP test.



7 ASTM WK68886: New Practice for Long-term evaluation of turbine oil performance to assess the antioxidant stability and deposit control

It is interesting to observe that even when most of the antioxidants have been consumed, the presence of Solvancer continues to provide the fluid with strong long-term deposit control characteristics.

The performance of Solvancer in extensive lab testing surpasses the other Solubility Enhancer chemistries that were studied. It provided both quick and sustainable long-term deposit control results. It is compatible with a wide range of formulations and does not contain any surface-active chemistry to interfere with the surfactants or the anti-wear chemistry. Another property that set Solvancer apart from the other Solubility Enhancing technologies is that it didn't contribute to any deposits in the fluid, even at temperatures of 250C⁸ while other fluid creates carbon deposits more than 0.1%

Laboratory testing are an essential part of the development of any new product, however it doesn't replace field testing.

Case Studies

The Solvancer technology has been tested in a range of applications under different stress levels and with various formulations. Below is a summary of a few of the case studies where traditional varnish mitigation technologies would not be an appropriate solution.

Coal Pulverizer Gearbox

A coal pulverizer, using an ISO VG 320 gear oil in a 110-gallon reservoir undergoes significant thermal degradation. The reservoir operates between 75-90C and the fluid is changed every three months. During the fluid change, significant effort is required to clean and flush the gearbox as it is covered with varnish. Analysis of the deposits revealed that it consisted of both soluble oxidation products and insoluble coal dust.

The plant treated the pulverizer gear oil with Solvancer to test if the oil drain interval could be extended and if the amount of sludge formation could be reduced.

8 ASTM D874: Standard Test Method for Sulfated Ash from Lubricating Oils and Additives

Figure 7: FTIR analysis revealed that the fluid was getting darker as a result of Solvancer dissolving oxidation products and suspended coal dust into the fluid.

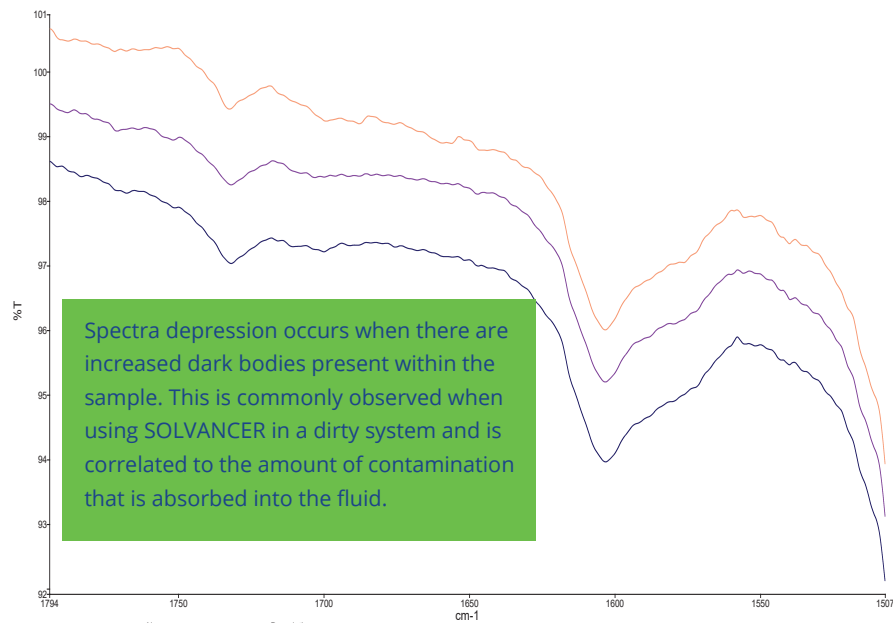


Figure 8: The color of the fluid darkened over the 3 months as part of the decontamination process as the sludge and coal dust were dissolved from the internals of the gearbox

Figure 9: Before Solvancer was added, the gearbox was heavily contaminated with varnish and coal dust. After Solvancer, only a small amount of coal dust was visible in the reservoir. There were no varnish deposits in the system internals.

Before Solvancer Treatment



After Solvancer Treatment (3 months)

Solvancer was shown to not only eliminate varnish formation in this thermally-stressed gearbox application but also allowed the plant to extend their drain interval from 3-months to 12-months.

Heavily degraded hydraulic oil used in a plastic injection molding machine

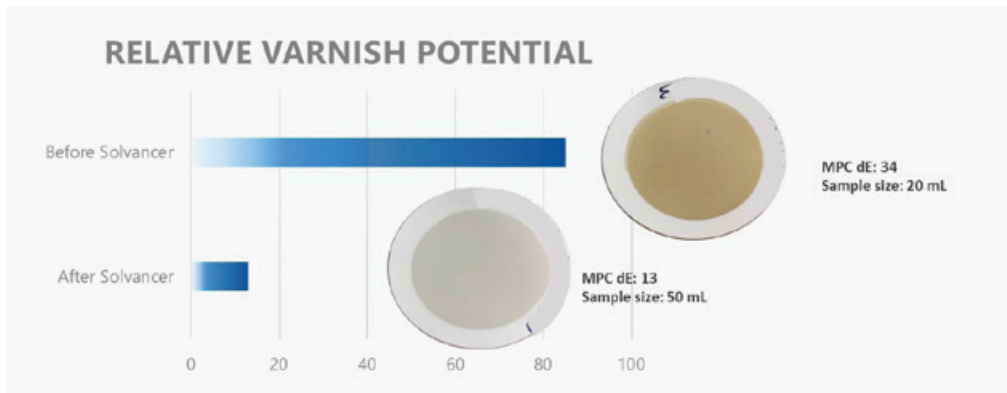
Plastic injection molding machines can be stressful environments for hydraulic oils to perform. Not only are they exposed to thermal stress, but the servo valves are intolerant to deposit formation. Varnish can cause significant reliability and production challenges in these machines.

Compounding varnish problems in this industry is the fact that varnish potential tests are often not included in oil analysis programs. When operators are not measuring, or even aware of varnish issues, the problem persists undiagnosed. Even those operations that are acutely aware of varnish, and have incorporated appropriate oil analysis tests, have challenges solving this issue. Although there are some varnish mitigation technologies that may be effective, installing side-stream filtration systems on every machine reservoir can be extremely costly.

A plastic manufacturer had a problematic machine where they wished to try Solvancer. A normal MPC test could not be performed on this fluid, as the 0.45µm membrane patch was blocked after only 20 out of 50mls of oil made it through the patch. The color of the patch was measured at a d₄₈₈ of 34.

Solvancer was added to this plastic injection molding machine. Over the course of a day, the varnish potential dropped considerably. During the MPC test, all 50mls of oil sample made it through the patch and the resulting color was a d₄₈₈ of 13. To provide a relative comparison of the before and after tests, the d₄₈₈ value of the before sample was adjusted to reflect the differences in filtrate volume, as can be seen in Figure 10.

Figure 10: Impact of Solvancer in hydraulic oil from a plastic injection molding machine. The initial sample had an MPC value of 24, however only 20 out of 50ml could be filtered through the patch. After treatment, all 50 mLs of hydraulic oil could be filtered.



Another varnish potential test that is often used on in-service oils is the Ultra-Centrifuge (UC) test. This method extracts soluble and insoluble material from the oil by spinning the fluid in a test tube at 17,000rpm. A visual assessment is made on the separated deposits and the fluid is given a rating on a scale between 1 and 8.

The addition of Solvancer to the in-service hydraulic oil showed a significant improvement in the UC test, as shown in Figure 11.

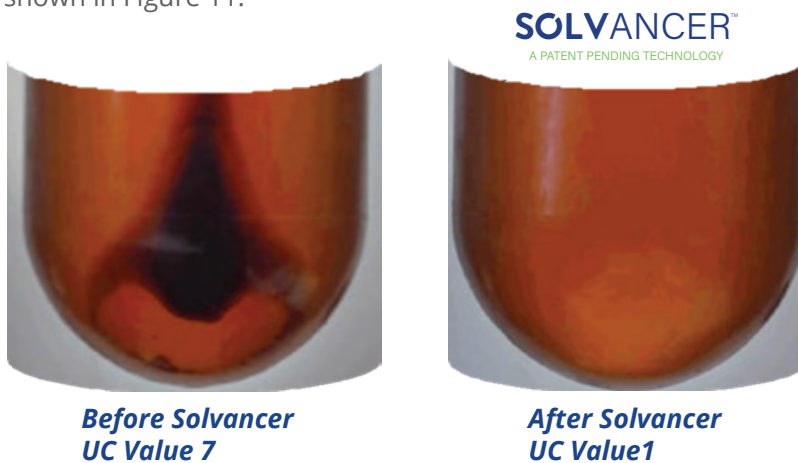


Figure 11: UC Values before and after the addition of Solvancer.

After treating the in-service hydraulic oil with Solvancer, the plant noticed an immediate improvement in clamp speed and cycle time. Furthermore, significantly less time was required during their next shutdown to facilitate a mold change-over.

CONCLUSION

Varnish is a significant reliability concern in a wide range of industrial lubricant applications. The traditional application of a kidney-loop filtration system using specialized media is not always a practical or economical solution. A new, scalable solution is required for these applications.

A Solvancy Enhancer referred to as Solvancer was developed. It is found to be compatible in a wide range of lubricants, including API GI to GIV basestocks. The technology does not use surface active ingredients for system cleaning, but depends on its ability to impart outstanding solubility characteristics to the in-service fluid. The fluid's solubility improvements allow it to dissolve soluble deposits, cleaning system internals. This process is done online while the system is in operation.

Solvancer was found to provide excellent long-term deposit control performance to lubricants, resisting deposit formation under severe oxidative stress, continuing even after the antioxidants had been consumed. In field applications, the use of Solvancer has been effective at both dissolving varnish from the internals of lube systems, and in protecting the fluid from generating further deposits.

SOLVANCER™
A PATENT PENDING TECHNOLOGY

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