European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids

CEC Investigative Report

Resinous Liner Lacquering

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Contents:

1. Introduction

In the early to mid 1980's service engineers reported complaints of high oil consumption in new engines. At the same time a few engine manufacturers identified the problem of cylinder liner lacquering in medium speed engines. On investigation it was found that the liners of these engines were covered in a transparent yellow to brown deposits. In some circumstances piston grove fouling and/or bore polishing were also reported.

This issue was brought to the CEC IL-21 Working Group in 1986 for detailed examination of the factors involved in the service problems. Two investigative reports were issued dated September 1991 (Ref [1]) and February 1993 (Ref [2]). This CEC investigative report provides updated information on the issue of high oil consumption, liner lacquering, piston crown land deposits, ring and groove deposits and severe liner damage involving scoring or polishing.

2. Current Status

Market information has confirmed that liner lacquer is still an issue in the industry, but the full extent of this issue is not known, since separated cases of liner lacquer are not routinely recorded. The experience is that coastal ships and fishing vessels are particularly susceptible, because these ships and vessels bunker frequently and this makes it hard to identify the actual fuel source responsible for liner lacquering.

It is also believed that the increase in engine operation with low sulphur fuel enforced by environmental bodies may increase the occurrences of liner lacquering in four stroke engines and even extend this problem to two stroke engines. This remains to be seen as the use of low S fuels increases in marine applications.

Analysis of liner lacquer is not available, due to the difficulties in obtaining liner lacquer samples. It is also difficult to obtain fuel which is proven to lead to liner lacquer formation, since there is no guarantee that the fuel in use when liner lacquer is observed is the same one that caused the problem in the first place.

Additionally it is quite hard to obtain any feedback from the field. Attempts to obtain answers, using surveys, from the ship operators in the 1990s proved to be not successful.

3. Identification of possible factors

Over the years several common factors have been identified in examples of liner lacquer formation. These factors are:

Loss of oil and higher oil consumption has been reported by engineers, when engines were operating on MDO and HFO. The common factor seems to have been running on low sulphur fuel. The factors contributing to high oil consumption are:

Fuel

1. Gas oil chemical composition (FBP > 450 deg C) (high polyaromatics content)
2. Gas oil with low sulphur content and cases have been reported with sulphur content up to 0.7% m/m
3. Residual fuel oil chemical composition (high polyaromatics content)
4. Residual fuel oil with sulphur content of less than 1.0% m/m

Lubricant

5. Quality of lubricating oil – some are better than others

Engine design/maintenance/operating conditions

6. Highly rated BMEP >18 Bar
7. Engine overload with MCR = 100% (temperature influence). Dutch fishing boats reported lacquering during the high load/low revolution

operation during trawling (the engine is not designed for overload, which affected the combustion)
8. Injection angle and quality of injection
9. Engine design (particularly liner temperature, cooling efficiency, type of turbocharger and the type of engine operation)

4. Proposed mechanism

Liner lacquer is described as a yellow to brown resinous material. The phenomenon of resinous liner lacquering is normally seen when ships are operating on distillate marine diesel fuel. A mechanism for liner lacquer formation has been proposed during CEC investigation (Ref [3])

Liner lacquering tends to be confined to situations in which the fuel final boiling point is in the range 420°C – 450°C, compared to a typical of around 340°C for non-lacquering fuel.

Liner lacquering is also normally seen when low sulphur fuel is in use.

Fuels with liner lacquering tendencies tend to be higher in aromatics (typically 40%+) and lower in paraffinics than fuels, which do not indicate such tendencies (which are more typically around 25% aromatics). (Ref[4]) (Ref [5])

The detection of a higher than normal final boiling point, may indicate a higher than normal content of polycyclic aromatic hydrocarbons (PAHs) in the fuel. There are hundreds of aromatic species present in marine fuel, but some of the more common compounds are:

Name	Number of linked rings	Boiling Point
Anthracene	3	340°C
Phenanthrene	3	340°C
Fluoranthrene	4	384°C
Pyrene	4	404°C
Benzanthracene	4	438°C
Naphthacene	4	440°C
Chrysene	4	448°C
Triphenylene	4	438°C

From the boiling points listed here, it seems likely that a significant difference between fuels having liner lacquering tendencies and those which do not, is the presence in the former of significant amounts of PAHs such as benzanthracene, naphthacene, chrysene, triphenylene, pyrene and many more related species. Furthermore it is likely that fuel with liner lacquering tendencies will also have higher levels of slightly lower boiling point PAHs such as anthracene and phenanthrene.

It is known that anthracene is readily oxidised at about 400°C in the presence of iron to anthroquinone. This process will also occur for the other PAHs. This

temperature is of course readily attained in the combustion zone, and the cylinder walls are a good source of catalytic iron. Once formed, anthroquinone and the other quinones formed from PAHs are relatively stable to further oxidation, even at high temperatures. Furthermore anthroquinone and some of the other quinones have high melting points (see the table below), which means that the quinones would be solids in the cooler parts of the cylinder. Therefore resinous lacquer formation could consist of partial oxidation of polycyclic aromatic hydrocarbons to the corresponding quinones in the combustion process at 400°C+, followed by deposition of these species as lacquer onto the cooler liner walls.

Name product	**No of linked rings**	**Boiling Point**	**Melting point of oxidation**
Anthracene	3	340°C	286°C
Phenanthrene	3	340°C	210°C
Fluoranthrene	4	384°C	272°C
Pyrene	4	404°C	
Benzanthracene	4	438°C	170°C
Naphthacene	4	440°C	285°C dec
Chrysene	4	448°C	211°C
Triphenylene	4	438°C	

The quinones are typically yellow to orange in colour, very similar to the reported colour of liner lacquer.

The quinones are also insoluble in most solvents (including diesel fuel and lube oil), but they *are* soluble in acids, such as sulphuric acid (and acetic acid). Therefore, when using high sulphur fuel, the sulphuric acid formed during combustion would help to solubilise the quinones and to wash the lacquer down into the crankcase oil. When using a low sulphur fuel, this effect would be much reduced, leaving the lacquer stuck to the liners. This fits quite well with the observation that liner lacquer is only a problem with low sulphur fuels.

5. Analysis of lacquer

Detailed analyses of the liner lacquer seem not to be available, hence the composition of the liner lacquer proposed in the earlier chapters have not been proved in practise. Infineum has some data that shows that the lacquer is made of a mixture of HC-materials and calcium sulphate, but no detailed analyses are available.

6. Recommendations

6.1) Detecting liner lacquer

Operators see a noticeable, steady increase in lubricating oil consumption, which cannot be explained by simple leakage.

A visual inspection can also be used, although this can sometimes be misleading. To overcome any uncertainty the surface should be washed with acetic acid (or vinegar), which removes the lacquer.

Another feature proposed by Barnes et al Ref [6] and Ref [7] is the measurement of surface roughness. The accumulation of liner lacquer fills the honing grooves, leading to a smoother surface. However, such measurement requires stopping and dismantling the engine, which may not always be possible in practice.

6.2) Dealing with liner lacquer/Cleaning methods

Liner rehoning is required to completely remove the lacquer, but cleaning with a suitable acid such as acetic acid can be a short term solution for partial removal of liner lacquer.

If the engine is switched temporarily to high sulphur fuel operation, the sulphur acids formed during combustion may dissolve the lacquer, giving a clean-up effect.

6.3) Preventive Methods

There are certain measures that can be taken to prevent or minimise liner lacquer formation and such measures have been described by Barnes et al Ref [6]. One such measure is to ensure good engine maintenance in co-operation with the engine manufacturer:

i) maintenance of fuel injectors (ensuring that they are clean and provide good atomisation of the fuel and that their position is well adjusted),
ii) maintenance/adjustment of the cooling around the liners (ensuring that liners are hot enough to prevent the condensation of the fuel on the liner) and
iii) maintenance of the turbocharger condition (preventing incomplete combustion).

Other factors affecting liner lacquer formation such as the level of sulphur in the fuel and the engine loading pattern (for example idle and part-load combined with full load, which is often seen in fishing boats) can be more difficult to control by the operator.

Use of alternative lubricants, which are specially formulated for liner lacquer/low sulphur fuel operation may also be recommended.

7. Conclusions

7.1) Liner lacquering continues to be an issue in medium speed marine engines
7.2) There are many contributing factors to liner lacquer formation
7.3) In-depth analysis of the lacquer is still needed

7.4) Feedback from the industry about the extent of the occurrence of liner lacquer is required to monitor the problems in the future
7.5) Knowledge of the problem is growing, hence this report is able to provide guidelines, which might help to reduce the frequency of liner lacquer formation
7.6) As a result of changes to European marine fuel environmental regulations, there is likely to be an increase in the use of the low sulphur fuels which can be one of the factors of liner lacquering
7.7) The industry must continue to be aware of the problem of liner lacquering and be watchful for any increase in the number of cases

8. References

[1] A.B.F. Bros, A. Verhelst, D. Voogdt - CEC Investigative Report on Liner Lacquering from CEC-IL-21 Working Group “Liner Lacquering” - 20 September 1991
[2] A.B.F. Bros (Stock-Wartsila Diesel), A. Verhelst (Texaco), D. Voogdt (Deutz MWM) and M. J. Cannon (Shell Research BV) – CEC IL-21 Investigative Report – Mechanism of Loss of Oil Consumption Control During Operation of Medium Speed Diesel Engines (Interim Status Report) – February 1993
[3] S.J.Cook, Lubrizol internal communications - October 1999
[4] R.W. Allen (Castrol International Marine) – The influence of marine fuel quality on lubricating oil performance - January 1995
[5] MER article – Lubes for Lacquers – November 2002
[6] J.Barnes, P.Berentsen, J.Hammett (Shell Global Solutions), Cylinder liner lacquering in distillate fuelled medium speed engines, CIMAC Congress, Kyoto 2004
[7] Shell Netherland publication – Formation and consequences of deposits on pistons and cylinders in medium and high-speed diesel engines – year 2000