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Methanol-fueled marine engine: combustion characteristics and new lubricant performance need

Lubricants

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ABSTRACT

The challenges surrounding the maritime energy and ecological transition are colossal and go far beyond the maritime domain alone because the latter is essential to the global economy. It ensures the transport of more than 80% of goods throughout the world, which are essential to the economy and populations.

Even though maritime transportation is more environmentally friendly in terms of emissions compared to other modes of transport, the quantity of goods transported by sea makes its overall impact significant. Currently, maritime transport accounts for 3 to 4% of global CO2 emissions. In fact, if international emissions were a country, maritime transport would rank sixth globally, emitting over 1,000 million tons of CO2 annually.

Like other industrial sectors, the maritime sector must accelerate its energy transition, especially since international and European regulations come into force in 2023 and aim or will soon aim for carbon neutrality by 2050. To succeed in this transition, maritime and energy players will have to make unprecedented investments, and this over a very short time, in a regulatory and technological context that is still very uncertain. Many efforts to reduce greenhouse gas (GHG) emissions from shipping focus on energy efficiency of the vessels and switching to carbon-neutral fuels.

Methanol is being considered as a potential solution for reducing greenhouse gas emissions from shipping. Methanol is a liquid fuel that is easy to handle and store at room temperature, its toxicity is also limited compared to other solutions.

To ensure optimal and lasting operation of both 2-stroke and 4-stroke marine engines running on methanol, the impact on the lubricant must be analyzed.

This study allows for the determination of specific constraints and performance requirements for the lubricant from observation and deep analysis of used lubricant from dedicated test engine and first vessel sailing on methanol. The development of a test plan representative of observed effects subsequently highlights the most suitable formulation environment. This test-and-learn approach accelerates research and the development of adapted solutions if needed.

On another side, depending on the engine load and the architecture, methanol dual fuel engine needs at least 5% in energy of diesel as pilot fuel. To minimize the use of this and to minimize the GHG emissions we worked on enhancing the methanol combustion characteristic through additivation. In addition, to ensure the durability of methanol use in engine, we develop a package to prevent loss of lubricity and corrosion.

1 INTRODUCTION

One way to reduce emissions from shipping is to switch from fossil fuels to renewable fuels. One alternative marine fuel that can be produced from renewable energy sources is methanol. Methanol has recently emerged as a promising fuel for maritime shipping [1,2], being considered a short- to medium-term solution for decarbonizing shipping operations [3].

More recently, methanol has gained attention due to its potential to significantly reduce emissions and its relatively easier integration into existing infrastructure compared to other alternatives fuels. A notable push for methanol as a marine fuel began around 2020, when the International Maritime Organization (IMO) approved guidelines for its safe use [4]. Since then, various reports and research have highlighted methanol's benefits compared to other alternative fuels, such as availability, energy density.

Compared to carbon-free fuels (hydrogen and ammonia), it requires lower storage volumes and simpler storage systems; hydrogen requires cryogenic conditions, whereas ammonia requires increased safety measures due to its toxic nature. Methanol sea transportation can be treated similarly to other liquid hydrocarbon fuels via product carriers as it remains liquid at ambient temperature. According to international guidelines, methanol is considered a highly flammable, high-toxicity fuel [5] [6]. When used as an engine fuel, methanol results in low emissions and in low environmental and health impacts [7].

2 IMPACT ON LUBRICANT

One of the specificities of methanol combustion is the formation of formic acids, unlike the usual fuel whose acid by-product is sulfuric acid. Methanol is also known to be sulfur free, toxic and corrosive. Burning methanol in a 2-stroke dedicated marine engine may require adapted specification for the Marine Cylinder lubricant (MCL), which must be determined either by observation in service as a fast-track method or by specific laboratory experimentation for a better understanding of the phenomenon of lubricant degradation and its resolution by selected additivation.

2.1 Observation In Service

As mentioned by DNV in its Energy Transition Outlook 2024 [8], methanol-fueled ships currently represent only 0.09% of the world fleet tonnage. Even though this technology is very popular, its global presence remains very limited, partly due to the availability of methanol. Thus, the currently available information from in-service return results is not plentiful.

Figure 1 below illustrates some results observed in the field on a ship equipped with the recent MAN Energy Solutions methanol-burning engine, the ME-LGI engine with the sort designation 7S50ME-B9-LGIM, referred to as Ship A. We were able to compare the behavior of the same commercial lubricant on a sistership equipped with a comparable engine, sort designation 7S50ME-B9-3, burning typical VLSFO, referred to as Ship B.

For both ships, Ship A and Ship B, the main engine is lubricated by the same commercial lubricant, which has general characteristics of TBN40, grade SAE50.

2.1.1 Results 1: Basicity

The international standard used to measure the basicity is the ASTM D2896, which uses strong perchloric acid ($HClO_4$) that can react with all basic species present in a lubricant formulation.

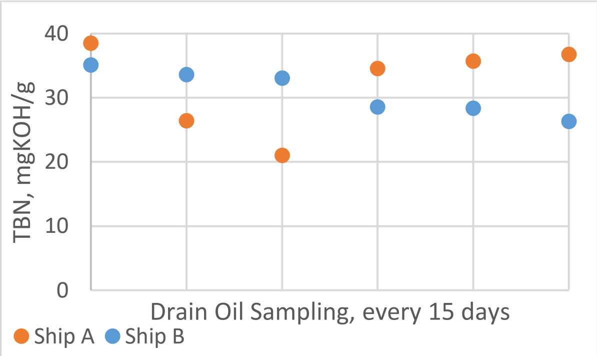

Figure 1. Residual TBN measurement

The TBN depletion for methanol-burning engine appears to be more significant and random.

2.1.2 Results 2: Viscosity

The international standards used to measure viscosity is the ASTM D665. As the two batches of lubricant did not start with the same viscosity, the results are normalized considering the evolution over the considered period for each sampling.

Figure 2 depicts the relative change in viscosity comparatively for the both ships.

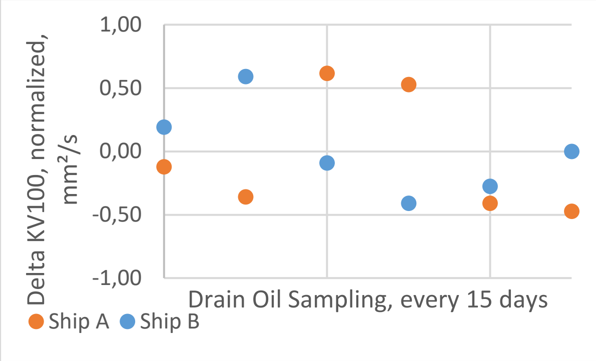

Figure 2. Drain oils - Viscosity measurements

There is no clear evidence of any difference between the two sets of drain oil samples.

2.1.3 Results 3: Wear - Iron content

The iron content of the drain oils reflects any wear that may occur in the contact between the piston-ring-liner. In Figure 3, the results of iron content are given for both ships.

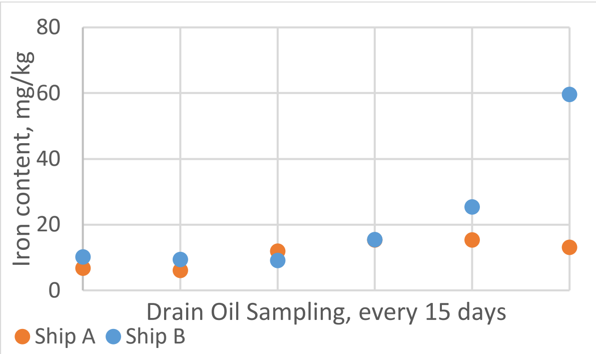

Figure 3. Drain oils – Iron content measurements

Ship B faced a problem with abnormal increase in wear, unrelated to the fuel impact. Apart from the last two samplings, no difference was observed between the ships.

2.1.4 Results 4: Wear – Chromium content

Chromium is known from the literature to be one of the metals that may suffer from methanol combustion engine.

Figure 4 highlights the comparative results of copper content for the two sisterships.

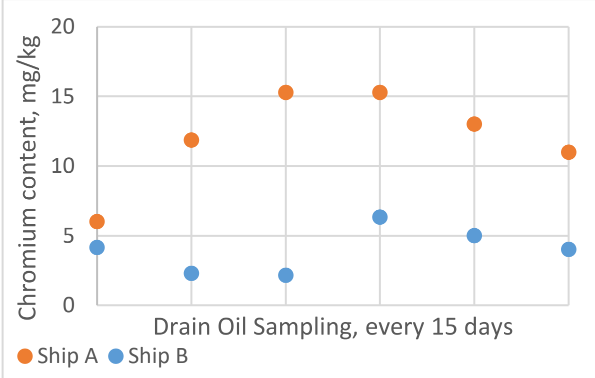

Figure 4. Drain oils – Chromium content measurements

Considering the chromium content level for both ships, there might be a tendency for Ship A, the methanol-fueled engine, to have higher levels than Ship B.

2.1.5 Observation in Service - Conclusion

The results observed in service will contribute to understanding the impact of methanol combustion on the behavior of cylinder oil in a two-stroke engine designed to burn this type of fuel. It is also through experimentation that we will develop our understanding of the phenomena to speed up the development of the lubricant formulas best suited to these new engines.

2.2 Simulation in the laboratory

A specific study was conducted on lubricant durability and performance retention in the presence of methanol combustion residue. The possible ingress of formic acid in the oil film must be addressed and neutralized by the basic species of the lubricant to protect the metal surfaces. This basicity reserve is mainly ensured by the detergent additives.

Basicity reserve is characterized by the TBN, ASTM D2896 potentiometric method.

2.2.1 Lubricant Degradation Mechanism

In an engine, there are two mechanisms of detergent degradation actions which impact potentiometric monitoring :

- Neutralization of acids formed by fuel combustion
- Thermal degradation impacting the basicity reserve

These two detergent degradation mechanisms occur in a methanol combustion engine. It is therefore advisable to have a good understanding of the specificities of methanol combustion (and more precisely the ratio between acid production and thermal degradation) to choose an appropriate combination of detergents for the formulation.

2.2.2 Neutralization Monitoring - Generalities

The classical and well-known behavior of a marine cylinder lubricant in a typical fuel-burning engine can be drafted as follows:

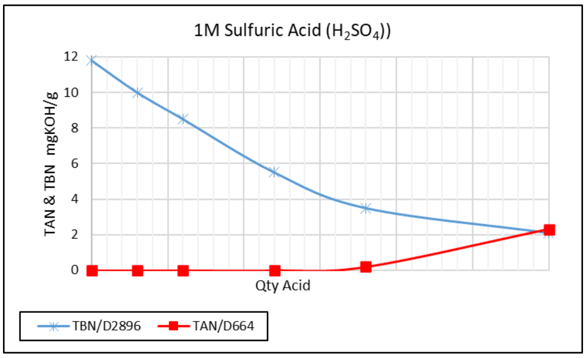

Figure 5. TBN/TAN titration curves

Several potentiometric methods can be employed. The acid neutralization capability of a lubricant is preferentially measured in two ways:

- Depletion of base in the lubricant (TBN, Total Base Number, ASTM D2896)
- Accumulation of acid in the oil (TAN, Total Acid Number, ASTM D664)

Sulfuric acid, produced during the combustion of conventional fuels, is neutralized by the detergent. Details of neutralization process are given [10], the TBN depletion is due to effective neutralization of H_2SO_4.

2.2.3 Neutralization Monitoring – Methanol Combustion Case Study

In the case of methanol combustion, its combustion product is mainly formic or methanoic acid, a weak organic acid [11], as illustrated by the general reaction below:

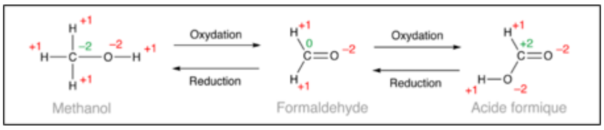

Figure 6. Methanol transformation

If we proceed with same measurement in a new environment, titration responses when acid is added give the following curves:

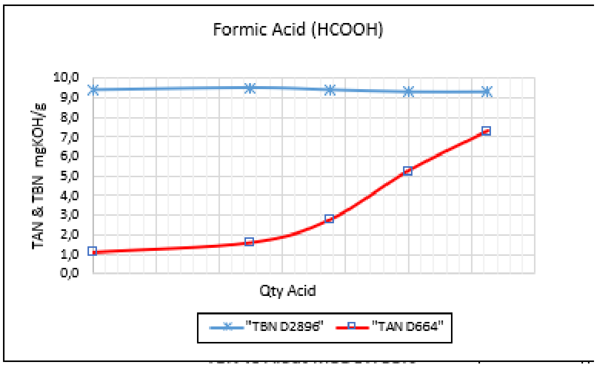

Figure 7. TBN/TAN titration curves

Different behavior is observed while adding formic acid.

- Little change in TBN D2896, almost no depletion
- TAN D664 increases throughout the test

The question arise, are organic acid neutralized. If we consider the overbased detergent which provides mineral calcium carbonate to neutralize the acids, the reaction for the neutralization is as follows [10]:

$$R\text{-}COOH + CaCO_3 \rightarrow H2O + CO_2 + Ca(R\text{-}COO)_2 \quad (1)$$

Acids are neutralized by the calcium carbonate, the overbased part of the detergent, leading to the formation of bases. Such bases, as well as remaining basicity are titrated by perchloric acid which is used in the TBN D2896 method. Therefore, neutralization of weak acids by detergent calcium carbonate base does not record as TBN depletion.

2.2.4 Thermal degradation

Thermal degradation also impacts the basicity reserve of the lubricant. An oxidation test, ICOT (Iron Catalyzed Oxidation Test, method reference GFC LU 36T03), was conducted to illustrate the phenomenon. The temperature of the test was set at 200°C for 48 hours with bubbling oxygen at 15 liters per hour. Three different detergent chemistries were compared, added in base oil group II (600R) with the target of TBN20 mgKOH/g. Results are given in the graph below, considering the variation of TBN in percentage:

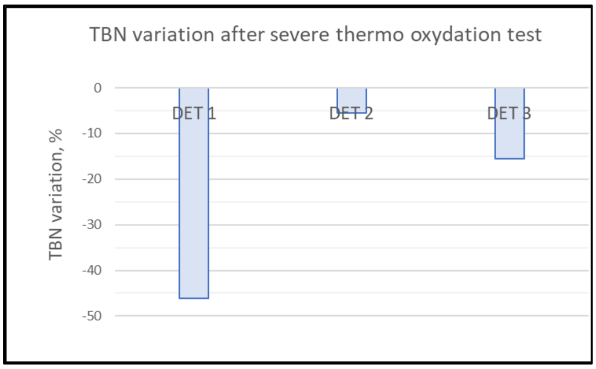

Figure 8. TBN variation after thermal degradation

We confirmed that thermal degradation contributes to TBN depletion, to varying degrees depending on the chemistry of the detergent.

2.2.5 Simulation in the Laboratory– Conclusion

The neutralization of formic acid by the overbased part of the detergent is not detected by the TBN D2896 method. Depletion of the TBN observed in engine is also due to neutralization and thermal degradation. Monitoring the TAN by the TAN D664 method seems mandatory to evaluate the basicity reserve of our lubricants and ultimately its protection against corrosion.

2.3 Degradation Process Monitoring – Methanol Combustion Engine

Field observations indicate a degradation of the lubricant, as evidenced by the depletion of TBN D2896. This study suggests that the TBN D2896 method does not accurately reflect the remaining basicity reserve of the lubricant.

Therefore, we infer that TBN D2896 primarily accounts for thermal degradation rather than the neutralization of weak acids formed during combustion. In contrast, TAN D664 provides insights into both the thermal degradation of the oil and the accumulation of acids.

Monitoring both TAN D664 and TBN D2896 allows us to better understand the aging phenomena of our lubricants, thereby aiding in the formulation of more effective lubricants for methanol combustion engines.

3 METHANOL COMBUSTION

Regarding the properties of the methanol, this fuel is well suited for spark ignition engines (SI) and not for conventional compression ignition (CI) diesel engines [12,13].

In the marine industry, one common method,to use methanol in CI engine is to design a dual-fuel setup using a pilot of diesel to pre-heat the combustion chamber which in turn helps ignite the methanol in the main injection [14]. In this configuration we need between 5 and 20% in energy of diesel depending on the engine architecture, size and load.

There is a possibility to decrease this energy ratio of diesel by improving the ignition property of the methanol using an ignition improver additive. The purpose of the ignition improver is to increase the cetane number of the blend, compared to neat methanol, and so promote ignition by compression. However, ignition improver is expensive, compared to diesel fuel and methanol, and should be kept to a minimum to be a viable option for maritime companies.

In the past studies [13, 15], we observe that an incorporation ratio of 3 to 5 percent of commercial ignition improver is necessary to use the methanol as a single fuel. With this order of magnitude, the additive is more becoming a co-base in the blend.

Our goal is to optimize the methanol/fuel energy ratio. The incorporation ratio of the ignition improver should also not exceed 1%.

3.1 Digital screening

The first step is to discover which molecules can be used as ignition improver. To do this, various calculations will have to be carried out to check the BDE (Bond Dissociation Energy) of the potential candidates. The BDE calculations are carried out with Gaussian software, which uses DFT (Density Functional Theory) calculations. This is a quantum calculation method that studies the structures and electronic properties of atoms and molecules. It is based on the principle of electron density and the spatial distribution of electrons. This software calculates the energy of the proton, the energy of the radical and then calculates the difference between these two energies and the total energy of the molecule.

In a second step we assess the solubility of the potential ignition improver with the methanol using COSMO suite. COSMO is first used to generate the sigma surface of the molecule and determine the electrostatic interactions of a molecule with a solvent to model the effects of solvation. Then COSMO-RS analyses the charge surface of the molecule to calculate chemical potentials in incompressible liquid phases at equilibrium based on quantum chemistry, and then the thermodynamic properties of the same molecule (such as the partition coefficient or the activity coefficient). Finally, COSMOtherm calculates the solubility between molecules using all the data previously generated.

With these two phases of computational chemistry, we found four interesting candidates.

3.2 Experimental set-up

The combustion properties of the methanol blends are measured in a combustion research unit (CRU). This instrument from FuelTech Solutions is used to both qualitatively and quantitatively study combustion fuel properties. Based on a well-established constant volume combustion chamber technology, the CRU can be set to a specified ambient condition to investigate different fuel characteristics (ignition delay, burn duration etc.) as a function of the process parameters (pressure, temperature, etc.). The limit of the testbench allow us to set ambient conditions close to the conditions in an internal combustion engine. A schematic diagram of the CRU can be seen in Figure 9.

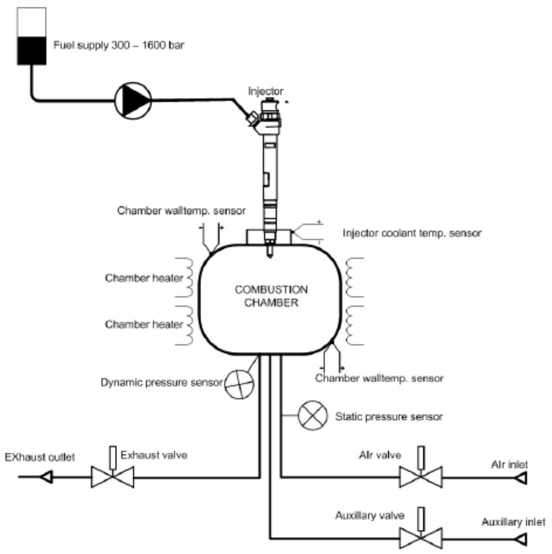

Figure 9. Schematic overview of the combustion chamber system

Due to the elimination of the engine dynamics (for example piston movement), the effects of varying fuel properties and compositions are much easier to be isolated and studied. The combustion chamber is filled with a mixture of synthetic air and pure nitrogen. The oxygen concentration can be regulated by the ratio of these two gases. Furthermore, it is equipped with an industry-standard common rail injection system. With a flexible modular design, the CRU is built of components and sub-systems (injection system and optical accessibility) that can be adapted to the specific research requirements. During the operation, fuel is directly injected into the pressurized and heated combustion chamber, where it meets the hot air and ignites.

The pressure trace of the combustion chamber after ignition is automatically recorded and saved by the software control system. With this data we can observe the start of combustion (SOC), the end of combustion (EOC) (refers to the time when 95% of maximum pressure is reached), the ignition delay (ID) (the time interval between the start of injection (SOI) and SOC) and the burn duration (BD) (time from SOC to EOC).

In addition, the rate of heat release (ROHR) is calculated using equation 2 based on first law of thermal dynamics:

$$ROHR = \frac{1}{\gamma - 1} * V * \frac{dp}{dt} \quad (2)$$

where V is the volume of the combustion chamber, dp/dt is pressure rise rate calculated from chamber pressure and γ the specific heat ratio which can be estimated. In this regard, the ROHR is nearly fully proportional to pressure.

For our measurements we used a specific setup with a dual fuel CRU to be representative of a marine architecture. This CRU comes with a second injection system, a GDI type injector that works with methanol. The pilot fuel system is still using the common rail type Diesel injector of the standard CRU.

This dual fuel setup enables experiments with varying injection strategies: 0-100% variable ratio between fuel A and fuel B, inject both fuels simultaneously or in a predefined order, variable injection timing and delay between injections.

Each injector may also be operated separately. The dual fuel CRU has then the same functionality as a standard CRU.

3.3 Fuel matrix

To allow good comparisons we used pure methanol, a blend with 1% of 2-Ethylhexyl Nitrate (2-EHN) as reference ignition improver (commercial additive) and three blends with the candidates A, B and C.

One of the candidates was not existing in any chemical suppliers. The decision was made to not synthetize it specifically for the test.

3.4 Results

We tested different temperature and pressure range. After processing of the data, we found that the following Figures 10 and 11 are the more representative of a dual fuel combustion after compression of the air in the engine.

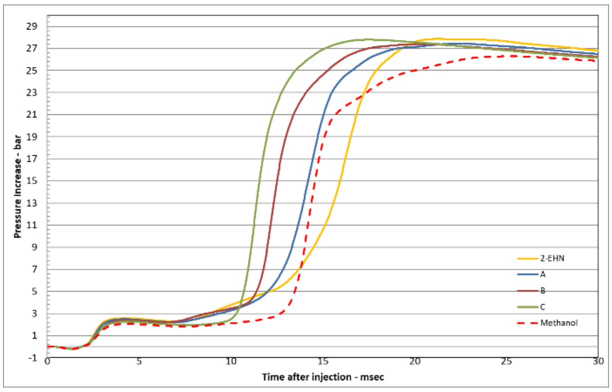

Figure 10. Combustion pressure trace at 550°C and 30 bar

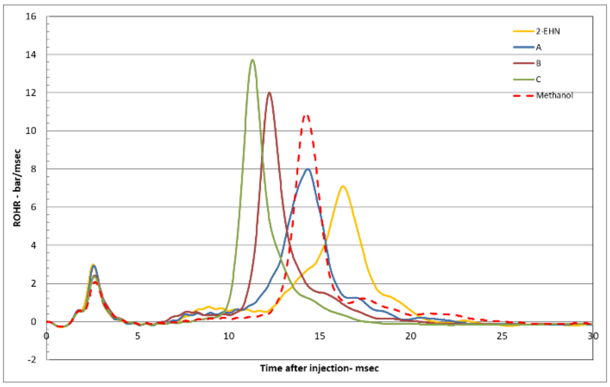

Figure 11. Rate of heat release trace at 550°C and 30 bar

We can observe in the Figure 11 a first small peak resulting of the pilot fuel combustion and a second bigger peak due to the methanol combustion.

We can see that at the incorporation of 1% the commercial ignition improver has not significant impact due to a partial premixed combustion. The ignition delay is quite good but afterwards the combustion is slower than with pure methanol.

Regarding our three candidates the more promising is candidate C. It has an ignition delay slightly higher than the others, but the combustion is quicker as the ROHR is higher and with a more constant combustion speed as we can see on the pressure trace. We can also see with the ROHR Figure 11 than the combustion timing is the earliest in the comparison with the other fuels. This can have a positive impact on the engine efficiency.

4 CONCLUSIONS

The results show that methanol combustion does not highlight the neutralization of weak acids in the same way as fuel combustion. Therefore, it is essential to monitor both TAN D664 and TBN D2896 to better understand lubricant aging and formulate more effective lubricants for methanol combustion engines.

With a comprehensive study we found a promising ignition improver for methanol at 1% incorporation ratio. This additive allows the optimization of the energy split in a dual fuel engine towards the methanol as low carbon fuel and can maybe have a positive impact on the engine efficiency. Next step could be to test this additive with an engine test bench.

5 ACKNOWLEDGMENTS

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