# September 2019



Booklet for ship crew members Precautions concerning change-over to 0.50% sulphur compliant fuel oils [First Edition] [English]



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### Foreword

In order to comply with the new sulphur limit for fuel oil used on board ships taking effect from 1 January 2020, residual fuel oils with sulphur contents of 0.50% or lower (hereafter, referred to as "compliant fuel oils" in this booklet) will be distributed globally and loaded on board ships. Consequently, the number of occasions where fuels for main engines or auxiliary engines are changed from conventional fuel oils to compliant fuel oils and actually used will increase.

ClassNK, having summarized the potential risks related to the changing over from conventional fuel oils to compliant fuel oils and the measures necessary to mitigate said risks, has decided to make this information available to the ship crew members who are actually responsible for such operations.

The purpose of this booklet is, therefore, to provide ship crew members on board going to bunker and actually use compliant fuel oils with information focusing on the "compatibility" and "cold flow properties" of such fuels as well as the risks associated with such fuels and the measures to be taken to mitigate such risks.

In addition, at our request, relevant recommendations and product leaflets for mitigating the potential risks of compliant fuel oils have been provided by several chemical makers pertaining to the sludge dispersants and sludge solubilizers that are referred to in this booklet. These materials are added as attachments to this booklet.

In cases where HSFO (High Sulphur Fuel Oil) has been stored in a ship's fuel oil storage tank before compliant fuel oil is loaded in the tank, on the other hand, sludge may precipitate on the bottom part of the tank or on the tank walls. In such cases, if a compliant fuel oil was loaded into the tank without due considerations, then it might lead to operational problems in the fuel oil purifiers, filters and engines, or sulphur content of the mixed fuel oil in the tank might exceed 0.50%.

In this regard, the development of a plan to manage fuel oils within a sulphur content of 0.50% or lower, including the preparation for fuel oil change-over by tank cleaning, is recommended; for example, the Ship Implementation Plan referred to in the IMO's *Guidance on the development of a ship implementation plan for the consistent implementation of the 0.50% sulphur limit under MARPOL Annex VI* (MEPC.1/Circ.878). When developing a Ship Implementation Plan, please refer to the sample plan that ClassNK has provided<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> Please refer to ClassNK Technical Information TEC-1179 for more information.

As possible countermeasures to sludge precipitating in storage tanks in which HSFO has been stored, cleaning the tank, dosing sludge dispersants multiple times before loading compliant fuel oils, loading LSMGO (Low Sulphur Marine Gas Oil) or dosing sludge solubilizers are things to consider. While it is understood that a number of ship operators have already developed such plans, those who have yet to do so should refer to relevant recommendations and leaflets provided by several chemical makers that are attached to this booklet.

Finally, since each ship has its own specific design, specification and operational condition, it is necessary for the shipping company to decide the preventive measures suitable for each ship based upon the technical information provided by the shipyards, manufacturers and chemical makers.

ClassNK hopes that this booklet will foster a common understanding of compliant fuel oils and contribute to management of such fuel oils among stakeholders, in particular ship crew members.

> 30 September 2019 ClassNK Machinery Department

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## 1 Risks associated with the changing over to compliant fuel oils

In the *Guidance for onboard use of Compliant Fuel Oil with SOx regulation from 2020*<sup>2</sup> issued by ClassNK in March 2019, the following five properties of residual fuel oils that should be further considered when using compliant fuel oil are explained.

- Compatibility
- Low viscosity
- Cold flow properties
- Cat-fines (contents of Aluminum and Silicon)
- Ignition and combustion quality

Among them, this time, particular focus is paid to "compatibility" and "cold flow properties" that are particularly relevant to the changing over to compliant fuel oils. In short, the issue of compatibility is the sludge formation due to incompatibility, and that of cold flow properties is the wax formation at low temperatures, i.e. solidification, respectively. Each of these is explained below.

#### 1.1 Compatibility

*Compatibility* is an index of how likely sludge will be formed when mixing two different types of fuel oils. Such mixing of fuel oils can be a complex issue, and even two types of fuel oils which are independently stable may lead to sludge formation when they are mixed together.

The following issues may occur as the result of excessive sludge formation arising from fuel incompatibility.

-1 Sludge precipitation in fuel tanks and pipes

Sludge formation may occur in storage tanks when different fuels are bunkered. Sludge formation may also occur in the settling tanks, service tanks or pipes when fuels for onboard machinery are changed to compliant fuels. In such cases, the presence of sludge can clog pipes and make fuel transfer impossible.

<sup>&</sup>lt;sup>2</sup> The aforementioned guidance is available to download free of charge via ClassNK's website <u>www.classnk.com</u> for those who have registered for the ClassNK "MyPage" service. To register for the "MyPage" service free of charge, go to the ClassNK website <u>www.classnk.com</u> and click on the "MyPage Login" button.

### -2 Plugging of fuel oil filters<sup>3</sup>

When sludge precipitated in the fuel tanks is transferred or sludge is formed in the piping systems, filters may be plugged or blocked. In such cases, the fuel supply to the main engine may be reduced, which, may even cause the main engine to stop in the worst case scenario. In addition, the fuel supply to auxiliary engines may also be stopped, which in turn may lead to blackouts.

### -3 Sludge accumulation in purifiers

When the plugging of filters is confirmed, it is indicative of a possible increase in the amount of sludge being captured by the purifiers. Excessive sludge sediment on the rotating parts of purifiers can generate an imbalance in such; therefore, the discharged of the sludge may lead to abnormal vibrations or result in damage to the purifiers.





Source: Guide for use of 2020 SOx regulation compliant fuel oils Provided by NIPPON KAIJI KENTEI KYOKAI (Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism of Japan)

## Figure 1.1: Sludge in fuel oil filters

### 1.2 Cold flow properties

In the case of compliant fuels with high pour points, wax crystal formation may start at low temperatures.

The following issues may occur as a result of wax formation.

-1 Wax formation in fuel tanks

When wax formation occurs in storage tanks, fuel transfer from the storage tanks to the settling tank via fuel oil transfer pump may become difficult.

-2 Choking of fuel pipes (particularly filters)

When wax formation occurs, it can lead to choking of fuel pipes, and the plugging or blocking of filters. In such cases, fuel supply to the main engine may be reduced which may even cause the main engine to stop in the worst case scenario. In addition, the fuel supply to the auxiliary engines may also be stopped, which in turn may lead to blackouts.

<sup>&</sup>lt;sup>3</sup> In this booklet, "filter(s)" includes strainer(s) as well.

#### -3. Wax accumulation in purifiers

When wax formation occurs and wax is accumulated in the purifier, the performance of purifier may be reduced which may result in an insufficient quality of fuel being provided to relevant machinery. In addition, it can lead to excessive wax sediment on the rotating parts of purifiers which can generate an imbalance in such parts; therefore, the discharge of the wax may lead to abnormal vibrations or result in damage to the purifiers.

Since compliant fuels are said to have a lower viscosity than the conventional high-sulphur residual fuel oil (HSFO), fuels that do not need heating may be available on the market. If such fuels are stored in storage tanks not provided with heating equipment, problems may occur within cold areas or during winter seasons because the fuel may begin to form wax which may in turn start to solidify.

Although reheating the fuel to above its pour point will dissolve the waxy precipitates, reliquefying such fuel tends to take a considerable amount of time due to the generally high latent heat of waxy precipitates. Since it is fairly difficult to dissolve waxy precipitates by adding chemicals, etc., it is important to put measures in place to prevent wax formation in the first place.



Filter blocked due to wax deposit Source: 01|2015CIMAC Guideline



Wax collected in a metal scoop Source: Guide for use of 2020 SOx regulation compliant fuel oils (Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism of Japan)

Figure 1.2: Wax formation in fuel oil

# 2 Measures for changing over to compliant fuel oils

# 2.1 Measures for sludge formation due to mixing of fuel oils (Compatibility)

## 2.1.1 Measures

Measures to prevent sludge formation due to the mixing of fuel oils or to prevent problems related to sludge formation in machinery are as follows:

-1 Changing over in fuel oil storage tanks

- (1) Empty tanks as much as possible before bunkering a new batch of fuel.
- (2) If mixing within storage tanks cannot be avoided, check compatibility by spot test (in accordance with ASTM D4740, and refer to pages 21 and 36 of this booklet) whenever possible at bunker time. If incompatibility is confirmed, then add sludge dispersant to the remaining fuel oil in the storage tank before bunkering.

Since compatibility may change over time and sludge may be generated after long periods of storage even when the results of initial spot testing were good, it may, therefore, be desirable to use sludge dispersant whenever different fuel oils are mixed.

## -2 Changing over in fuel oil pipelines

When changing over in fuel oil pipelines in order to change-over to compliant fuel oil that is stored in a storage tank, the different types of fuel oils are generally mixed together in settling or service tanks, as shown in figure 2.1.

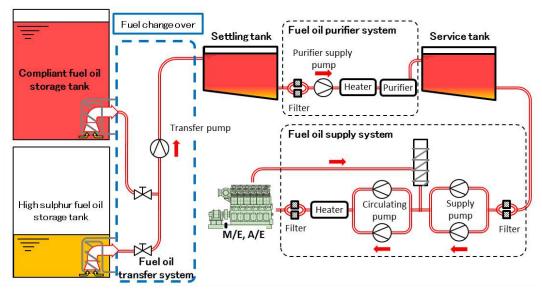


Figure 2.1: Fuel oil piping diagram

Measures to be taken in this case are as follows:

- (1) In order to avoid the mixing of different types of fuel oils in settling/service tanks, keep the amount of the remaining fuel oil in such tanks as minimal as possible, and then transfer compliant fuel oil from a storage tank to the settling/service tank.
- (2) Carry out a spot test, and, add a sludge dispersant to the settling tank if incompatibility is confirmed.
- (3) Use up the fuel oil which had been mixed together in tanks or pipelines as soon as possible.
- (4) In the cases where sludge is frequently confirmed in fuel oil pipelines or where the differential pressure in the pipeline between before and after the filter rises sharply, take the following actions:
  - i) Shorten the interval of backwashing;
  - ii) Keep the differential pressure of backwashing lower; and
  - iii) Clean the filter more frequently than usual.
- (5) In cases where sludge is frequently found in filters placed before purifiers, precipitation of sludge in the fuel oil purifier is also suspected. If a large amount of sludge generation is expected, take the following actions in order to avoid sludge accumulation on the separating disc of the purifier and to also improve separating efficiency:
  - i) Reduce the flow rate. It is also recommended to operate two sets of purifiers in parallel and to treat half the amount of fuel oil by each purifier;
  - ii) Shorten the interval of discharge of sludge;
  - iii) Maintain a high temperature of oil flow in accordance with the purifier manufacturer's manual; and
  - iv) Shorten the maintenance interval of the separating disc.

### 2.1.2 Cautionary notes

- -1 When changing over to compliant fuel oils
  - (1) In order to avoid serious accidents that may occur if the main engine fails, <u>do not</u> <u>carry out the changing over to compliant fuel oil in fuel oil pipelines while the</u> <u>ship is operating in congested sea areas or narrow water channels.</u>

- (2) Changing over to compliant fuel oils in fuel oil pipelines should be carried out <u>during the daytime, not at night</u>, so as to ensure there are enough crew members readily available to solve potential problems; and
- (3) Before changing over to a compliant fuel oil, clean the purifiers and filters. Keep purifiers and filters in a clean condition in order to identify whether any sludge, if confirmed, had been formed prior to the changing over or as the result of the changing over.

## -2 Flushing by sludge solubilizer or MGO

- (1) Before bunkering compliant fuel oils, ships may plan to undertake the flushing of storage tanks, settling/service tanks and fuel oil pipelines. In such cases, sludge that has been deposited on the bottom of such tanks or pipelines may flow out to pipelines in large quantities and clog purifiers and/or filters.
- (2) In cases where large amounts of sludge actually flow out, the sludge should be removed by purifiers and/or filters, as it is difficult to deal with using chemicals. In such cases, take the actions prescribed in paragraphs 2.1.1-2(4) and 2.1.1-2(5).

## 2.2 Measures to prevent wax formation in fuel oils (Cold flow properties)

-1 As for paraffinic compliant fuel oils and MGOs, the risk of the wax formation can be mitigated by heating. Proper heating of fuel oils is, therefore, useful as a precautionary measure.

In cases where the cold filter plugging point (CFPP: refer to page 11 of this booklet) of the fuel oil is known, heating the fuel oil above the CFPP is recommended.

In cases where the CFPP is not known but the pour point (PP: refer to page 11 of this booklet) is known, heating the fuel oil at least  $10^{\circ}$ C above the PP is recommended.

- -2 In cases where both the CFPP and the PP are not known, whether the fuel oil forms wax at a lower temperature can be confirmed by taking a sample of the fuel oil and keeping it in a refrigerator. It is desirable to set the temperature of the refrigerator to be the same as the temperature that the fuel oils are exposed to in the storage tank.
- -3 Fuel oils having lower viscosities and higher pour points might be distributed; in such cases, attention should be paid when using such fuel oils. As it is essential to ensure that the viscosity of fuel oil at the entrance of the main engine is as recommended by the engine manufacture, the temperature of the fuel oil may need to be kept within a narrow range.

- -4 If no heating equipment is provided in a fuel oil tank, it is recommended to use the fuel oil after confirming that the ambient temperature (seawater temperature and/or engine room temperature) is more than PP +10°C in consideration of the route and the climate. If it is not possible to ensure such a condition, using an additive to mitigate any wax formation may also be an option.
- -5 If wax is frequently confirmed in filters placed before purifiers, then take the actions as prescribed in paragraphs 2.1.1-2(4) and 2.1.1-2(5).

Attachments

# Attachment 1

Explanatory note on compatibility and cold flow properties

### Explanatory note on compatibility and cold flow properties

### 1 Compatibility

#### 1.1 Meaning of stability

"Stable" or "unstable" refers to whether sludge formation may occur. If no sludge is formed, the fuel is considered stable. Sludge is also sometimes referred to as "asphaltenic sludge" because the causal material is asphaltenes, the heaviest hydrocarbon compound in fuels. While compliant fuels in this booklet are categorized as residual fuels (Residual in ISO 8217:2017) and some are low viscosity and low density fuels, they more or less contain residue, and asphaltene is certainly contained in such residue.

Fuel oils consist of asphaltene, paraffinic hydrocarbon and aromatic hydrocarbon. The asphaltene in compliant fuel oils is expected to be only a few percent, depending upon the fuel oil in question. Asphaltene is more stable and less likely to form sludge in high aromatic fuel oils.

#### 1.2 Compatibility

The causes for sludge formation due to incompatibility are briefly explained hereafter. As noted above, asphaltene leads to sludge, and is usually dispersed in a fuel oil in the form of ultra-fine particles that are not visible even under a microscope. Under such stable conditions, asphaltene can be fully burnt after injected into an engine. Sludge, on the other hand, refers to the situation in which a large amount of asphaltene has coalesced into large visible particles.

As previously stated, a compliant fuel oil contains paraffinic and aromatic compounds in addition to asphaltene. To keep ultrafine asphaltene particles stable, it is necessary to create a condition in which the ultrafine asphaltene particles are scattered and in suspension surrounded by aromatic components.

When a considerable amount of paraffinic content is mixed together with such a stable fuel oil, the asphaltene becomes unstable due to the reduced amount of aromatics after the mixing; it, therefore, starts to aggregate and form sludge. This is called incompatibility.

Due to there being more methods for producing compliant fuel oils than there are for producing conventional high sulphur fuel oils, compatibility is expected to become a significant concern because of the anticipated wide distribution of fuel oils which contain a high amount of paraffin (i.e. "high-paraffinic fuel oil"). It should be noted that a property statement may not indicate whether the fuel oil in question is paraffinic. On the other hand, the CCAI values on property statements tend to be higher when fuel oils contain rich aromatics. It should be noted that, while aromatic component contributes to a fuel oil in stable condition, it may hamper ignition and combustibility.

MGO (marine gas oil), is also a highly paraffinic fuel oil, but it does not contain asphaltene; so, it is categorized as a distillate fuel oil. However, when an MGO is mixed into a residual fuel oil, it may make the asphaltene in the residual fuel oil unstable.

#### 2 Cold flow properties

In cases where compliant fuel oils are high paraffinic, their pour point becomes higher and wax may therefore form in cold climates, etc. if storage tanks are not provided with heating equipment. Wax formation is a phenomenon in which paraffin crystallizes at a low temperature and then starts to solidify. Even MGOs that do not contain any residual content may form wax because they contain a large amount of paraffin.

Wax formation is not associated with asphaltene. Wax is different from asphaltene sludge, and is also referred to as "wax sludge".

With respect to cold flow properties, particular attention should be given to the pour point of the fuel oil (Pour point, PP, in ISO 8217:2017). In cases where the temperature of a fuel oil is lowered below its pour point, the fuel oil begins to form wax and loses liquidity. In addition, at the temperature of Cold Filter Plugging Point (CFPP), which is generally 3-5°C higher than the pour point, waxes could actually clog filters in pipelines. In ISO 8217:2017, the upper limit for the pour point of residual fuel oils (except RMA and RMB) is prescribed as 30°C. So, if a fuel oil with a pour point close to 30°C is bunkered on board a ship, the possibility of wax formation in storage tanks and fuel oil pipelines under cold conditions, e.g. cold areas or winter seasons, will increase.

# Attachment 2

# Documents provided by NIPPON YUKA KOGYO CO., LTD.

Sludge dispersant fuel oil additive "YUNIC 555D" – Fuel oil tank pre-conditioning for changeover to low sulfur fuel

Yunic 800VLS Suppress sludge formation caused by poor compatibility of VLSFO

Wax Breaker – Fuel oil additive for improving cold flow property of MGO and MDO

Oil test kit YT type Spot checker – Test kit for TO compatibility and stability

Yunic 750LS-F A lubricity improver and microbial inhibitor for low-sulfur gas oil and heavy oil (bunker A)

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# Sludge dispersant fuel oil additive "YUNIC 555D " Fuel oil tank pre-conditioning for changeover to low sulfur fuel

Dear Customer,

Thank you very much for using Nippon Yuka's product on board your good vessel.

GLOBAL SULFUR CAP, an upcoming tight sulfur restriction starting from 1st of January in 2020, this restriction will impose minimum airborne emissions on all vessels in service, ship without an installation of effective exhaust gas scrubber must use the compliant fuel – fuel oil with less than 0.50% sulfur content in general sea area.

In respect of trouble-free changeover to low sulfur fuel oil, It is highly recommended conducting pre-tank conditioning with fuel oil additive YUNIC 555D, which successfully disperses the sedimentary asphaltene oil sludge, as a part of fuel oil managements on board. this results in maintaining the purification in fuel oil storage tank and also help to minimize the risk of sludge formation caused by the mixing of fuels with different properties.

#### **Dosing information \***

In a practical manner, YUNIC 555D should be dosed directly from the sounding pipe prior to the bunkering for the full dispersive effect to the fuel treated, while an adequate sludge dispersion is also obtained even though YUNIC 555D is dosed after the completion of bunkering. If using YUNIC 555D to clean the fuel oil tank that a sludge dispersant type chemical has not been used for a long period of time (or never been used before), be aware that the dispersion effect of YUNIC 555D may cause the sediment sludge to flow excessively, results in the FO strainer blockage. (Refer to the following dosage chart as a direction for use.). Also note that YUNIC 555D's sludge dissolving power becomes much more powerful as the dosage increased, along with the potential risk of FO strainer blockage, ship should adjust the dosage of YUNIC 555D accordingly while monitoring & checking the condition of FO strainer, especially for the FO tank in use.

Lastly, please note that the sludge dispersion effect when blended with fuel oil depends upon the fuel oil specification used and the property / condition of sediments to be cleaned.

	Recommended dosage to untreated tank					
Month(s) left before changeover	Dosing Rate	YUNIC 555D (L)	Fuel treated (MT)			
6 months before bunkering LSFO	1 / 20,000	1	20			
3 months before bunkering LSFO	1 / 8,000	1	8			
1 month before bunkering LSFO	1 / 4,000	1	4			

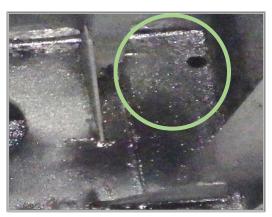
#### Pictures (1)

#### 1. Untreated tank inside



Sedimentary oil sludge at the edge of tank / between the floor space and wall surface.

#### 2. Tank treated with YUNIC 555D



Tank condition inside maintained clean. Ship had dosed YUNIC 555D with 1/20,000 for 3 months and continued with 1/8,000 for 2 months.

This document, and more, is available for download from Martin's Marine Engineering Page -.www.dieselduck.net contact your nearest sales representative if you require any further information.

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> An sample of the inside of a fuel tank when using the sludge dispersant "Yunic 555D"

#### Pictures (2)

1. Tank sidewall (From the bottom)



3. Tank sidewall and heating coils (From the top)





4. Heating coils close-up



## INFORMATION

Ship built in Type of ship Tank inspected Inspected in

: 2011 : LNG Carrier with Diesel Engine : HFO storage tank : 2019

#### **CONDITIONS**

Tank had been treated with YUNIC 555 since ship's delivery in 2011. Despite the long HFO storage period, tank was almost perfectly clean with only a small amount of asphaltene sludge remaining inside.

# Yunic 800VLS

# Suppress sludge formation caused by poor compatibility of VLSFO

**Yunic 800VLS** is a fuel oil additive for VLSFO (Fuel oil with sulfur content of 0.50% or less) that suppresses the generation of sludge due to poor compatibility when switching and commingling of VLSFOs. It contributes preventing sludge formations in fuel oil tanks, strainers, purifiers and fuel oil piping.

# **Advantages**

The global 0.50% sulphur cap will enter into force in 2020. The use of low sulfur fuel oil such as VLSFO is required after 2020 (except vessels with scrubber installations). It is said that the properties of VLSFO are more diversified than the high sulfur heavy fuel oil because the production method and blending method are considered to be different depending on the various region.

VLSFO may suppress sludge (caused by asphaltene and paraffin (wax)) if the compatibility is poor. As with high sulfur fuel oil, the generated sludge needs to be suppressed more strongly to prevent problems, such as sludge deposition in FO tank, FO strainer clogging and purifier malfunction etc.

Yunic 800VLS effectively suppresses the sludge generated from VLSFO and contributes to the prevention of sludge formation due to the poor compatibility (Sludge may be generated not only when commingling but also when used alone).



Image1 No sludge formation in compatibility of VLSFO (sludge does not occur)



Image2 Sludge formation in poor compatibility of VLSFO (flocculated sludge is formed and deposited at the bottom)

# **Direction for Use**

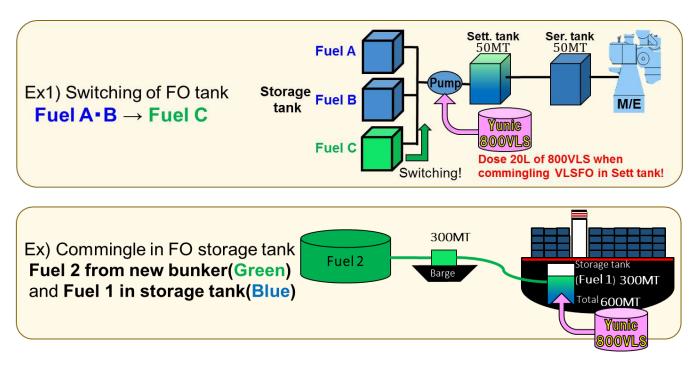
After checking the compatibility(stability) of VLSFO or HFO by Spot checker, if the evaluation is 3 or higher (may occur sludge trouble), we recommend dosing Yunic 800VLS.
 (For details of Spot checker, please refer to the next page or the instruction of Spot checker)

 $\Box$  Standard dosing rate is "1/2000". (50 liters for 100MT of fuel oil)

□ Please dose Yunic 800VLS to FO storage tanks if bunkering to FO storage tanks, or to the setting tank if the fuel oil is switched or commingled.

Please dose Yunic 800VLS referring to the illustration on the next page.

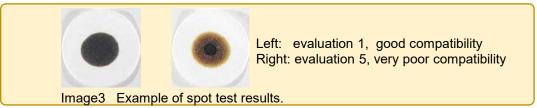
(Yunic 800VLS has good mixing with fuel oil like other Yunic series).



□ How to check compatibility (stability) on board:

Prepare (①)bunker FO sample, (②)FO sample remaining in FO tank of the ship, mix both (①+②) 50:50 FO sample, and carry out "Spot Test". (Reference product: Nippon Yuka Kogyo oil tester Spot checker)

- □ Sample (①+②) is the compatibility by Spot test. (As a reference, Sample (①) is the stability of the fuel oil alone) If the result "Evaluation 3~6", we recommend to dose Yunic 800VLS because there will be a possibility of sludge formation.
  - X Please refer to the oil tester YT series instruction manual for the fuel oil spot test procedure.
  - We provide technical service and advice such as spot test judgment, confirmation of the necessity of dosing Yunic 800VLS, and analysis of VLSFO.



# **Statement of fact and Patent**

- □ Nippon Yuka Kogyo had acquired the "Statement of fact" from ClassNK in March 2019.
- □ Patent(Japan) pending on April 2019 (PAT.P 2019-086571)
  - Title of invention: Fuel additive composition for fuel oil and fuel oil composition

# Container

- 200 Litter drum
- 18 Litter can
- Wight, kgSize, (W x D x H,cm)Approx. 204 $\phi$  58.5 x 89

Approx. 17.6 23.8 × 23.8 × 35



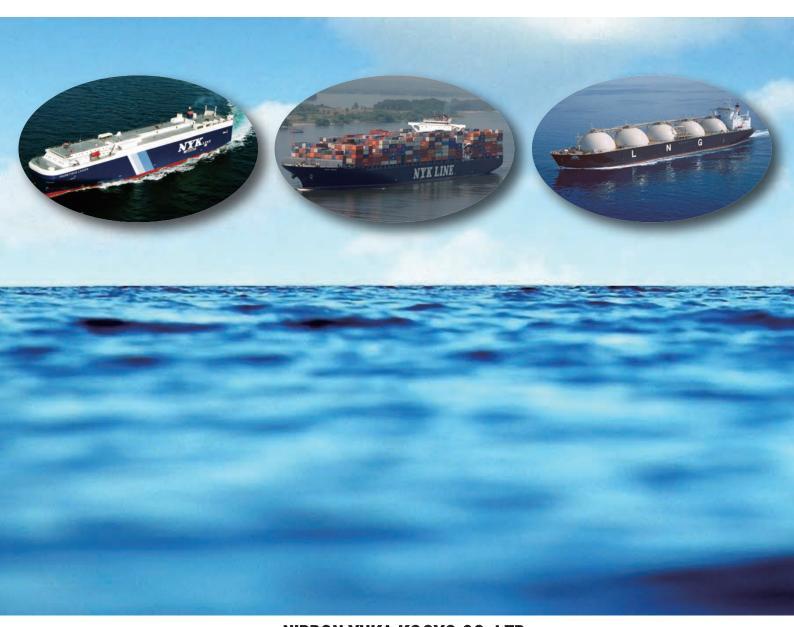
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# Wax Breaker

Fuel oil additive for improving cold flow property of MGO and MDO





# NIPPON YUKA KOGYO CO.,LTD.

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# Product Details

# **Characteristics**

- Appearance : Light yellow liquid (transparent ~ cloudy) : 20~30 mm<sup>\*</sup>/s@50℃
- :890~920 kg/m@15°C Density

Flashpoint : 66°C (PM closed cup tester)

Main components : Surfactants, polymeric materials, petroleum solvents

# **Properties**

On winter voyages or voyages from warm to cool regions, falling temperatures in fuel oil tank may cause solidification of fuel oil that has poor cold flow property, making it not able to be pumped. Wax Breaker is a fuel oil additive for improving cold flow property to prevent and correct fuel oil problems under cold temperatures (such as solidification of fuel oil in tanks or piping). The properties and effects of Wax Breaker are described below.

Flow property improvement (cold filter plugging point [CFPP], pour point [PP]) The PP of various types of marine gas oil (MGO) and marine diesel oil (MDO) is greatly improved by Wax Breaker. Although the standard dosing rate is 1/2000, improvement of the CFPP can also be expected by dosing 1/2000 to 1/500 (recommended dosing rate) of the amount of fuel oil as needed.

# Method of use

- The cold flow property (CFPP, PP) of various types of MGO and MDO can be improved by dosing Wax Breaker at a standard dosing rate of 1/2000 of the amount of fuel oil.
- Note : Depending on the type of fuel oil, dose 1/2000 to 1/500 (recommended dosing rate) of the amount of fuel oil.
- Dose Wax Breaker during bunkering of fuel oil or before the fuel oil solidified (while in a liquid state with sufficient flow property).
- Note : Wax Breaker is an inhibitor of fuel oil solidification but does not dissolve fuel oil that has already solidified. Therefore, it should be dosed by mixing it into fuel oil before it solidifies due to low temperatures.
- Although Wax Breaker has good mixing performance with fuel oil, optimal mixing is obtained by first dosing Wax Breaker into the fuel oil storage tank before bunkering.

# Precautions for use

- Flammable. No open flames.
- Wear protective equipment such as goggles, mask and oil-resistant gloves.
- First aid measures
  - In the event of eye contact, immediately flush with plenty of water for at least 15 minutes.
  - In the event of skin contact, wash well with soap water and apply skin cream.
  - In the event of vapor inhalation, move to a well-ventilated area and keep the body warm. \* Seek medical treatment as necessary.

# Storage precautions

- No open fire Store in a cool, dark place
  - Do not store at 50 °C or above or below 0 °C. The product may freeze partially when stored near 0°C. If partial freezing occurs, bring up the temperature of the product to room temperature before use.

# Packing

• 200 L drum

18 L oil can

- Weight : 201.5kg • Weight : 17.4 kg
- Dimensions :  $\varphi$  58.5cm  $\times$  89cm

 $\bigcirc$  Dimensions (W×D×H): 23.8cm×23.8cm×35cm

This document, and more, is available for download from Martin's Marine Engineering Page - www.dieselduck.net

# Wax Breaker

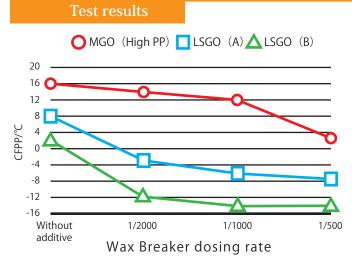
# A fuel oil additive that improves cold flow property and prevents problems caused by solidification of fuel oil.

In recent years, various problems related to cold flow property have occurred due to cold filter plugging and solidification of fuel oil in fuel oil tanks at low temperatures. This is caused by the paraffin wax (long straight-chain hydrocarbons, etc.) in the fuel oil crystalizing into a solid and precipitating at low temperatures, which causes the fuel oil to lose flowability overall. International standard for specification of marine fuels (ISO 8217 2017) set standards for the PP of MGO and MDO, which are distillate oils. However, they do not set standards for the CFPP, which is an indicator of when filter plugging actually occurs. Wax Breaker improves cold flow property and prevents the problems of plugging of strainers and purifiers and solidification of fuel oil when added to MGO and MDO.

# **Improvement of CFPP and PP**

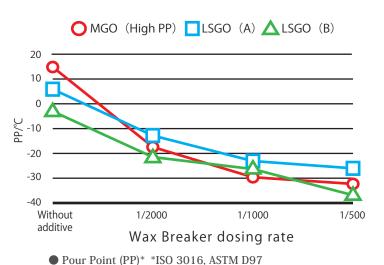
Fuel oil that has a high CFPP tends to contain a lot of materials with a high melting point (such as paraffin wax). As a result, when it is used at low temperatures, the precipitated wax components block strainers and piping, raising concerns about the possibility of blackouts and other problems. Results of investigations into the improvement effect of Wax Breaker on cold flow property have confirmed that the CFPP of all fuel oil can be reduced by at least 5°C by dosing Wax Breaker to MGO and LSGO at a ratio of 1/2000 to 1/500. (The standard dosing rate\* is 1/2000.) Furthermore, it has been confirmed that the PP of the fuel oil can be reduced to -10°C or lower by adding Wax Breaker to MGO and LSGO at a rate of 1/2000 or more.

\*Dosing rate assuming usage conditions with a minimum temperature of 5°C in the engine room





The procedure is repeated, as the specimen continues to cool, for each 1°C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipet exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was competenced is second at the CEPP terms of the



After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

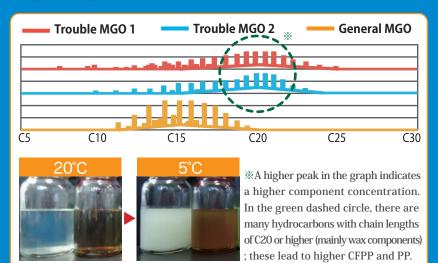
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# **Causes of Cold Flow Property Problems**

This shows the results of GC-MS analysis\* of general MGO and MGO in which cold flow property problems (strainer blockage) occurred. Whereas the main constituents of general MGO are hydrocarbons with chain lengths of C13 to C18, the components that are contained in the trouble MGO contain an extremely large amount of hydrocarbons with chain lengths of C20 or higher (melting point >  $30^{\circ}$ C). These components (wax components) have a high melting point and crystallize easily, and cause blockages in strainers and pipes.

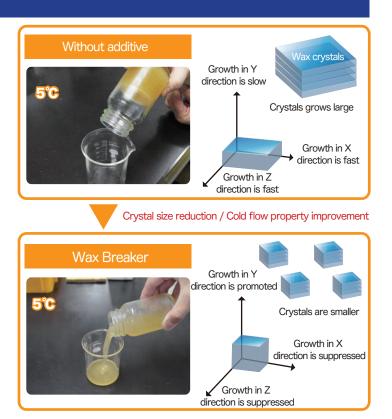
GC-MS analysis: gas chromatography-mass spectrometry

This is an analysis method that separates each of the components in an unknown sample and identifies the type (quality) and concentration (quantity) of each component.



Precipitation of wax components

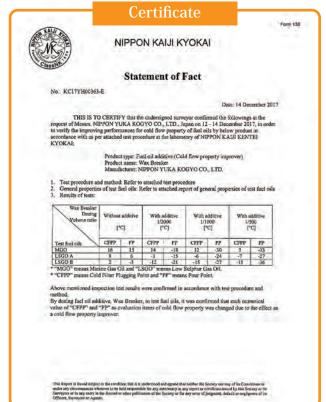
# Mechanism of cold flow property improvement



Below their melting point, the wax components in the fuel oil form crystals that grow in layers with the molecules arranged regularly. However, when Wax Breaker is added to improve cold flow property, it is incorporated between the crystal molecules and suppresses the crystal growth, thus improving the flowability of the liquid.

## Investigation of cold flow property improvement effect by third-party organizations

The cold flow property improvement effect of Wax Breaker has been investigated by third-party organizations. It was confirmed that the CFPP and PP are improved by addition of Wax Breaker to the MGO and LSGO used in the investigation, and a certificate (Statement of Fact) has been obtained from Nippon Kaiji Kyokai (Class NK).



This document, and more, is available for download from Martin's Marine Engineering Page - www.dieselduck.net

# Oil test kit YT type Spot checker Test kit for FO compatibility and stability

**"Spot checker"** (Fuel oil spot test kit: FO compatibility test) is a portable test kit to check the compatibility (stability) of heavy fuel oil including very low sulfur fuel oil (VLSFO). As the example to check, mixing of VLSFOs (fuel oil with sulfur content of 0.50% or less), mixing of VLSFO and ULSFO (or LSGO), VLSFO itself, heating and long-term storage, without limiting the measurement location.

# Outline

As for VLSFO after 2020, there is concern about compatibility. ISO PAS No.23263 (ISO8217) and the industry guidance including CIMAC (Joint Industry Guidance) describe the stability and compatibility test and confirmation method of comliant fuel oil (as of September 2019).

If judged not good after carried out FO spot test using by "Spot checker", it may cause sludge problems in FO strainer, FO tank or FO purifier.

We recommend "Yunic800 VLS" to prevent sludge troubles against compatibility promlem for VLSFO or the other compliant fuel oil.

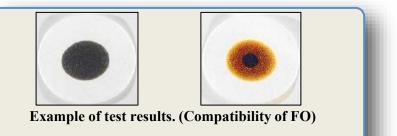
# Advantages

1) "Spot checker" is based on the standard ASTM D 4740 (Compatibility of residual fuels by Spot Test).

- 2) It is easy to carry and easy to use / operation (Only 100 AC outlet is required).
- 3) Please refer to "Reference photos for fuel oil spot test evaluation (Photo document: Not for sale)" enclosed in the test kit to eveluate the result of FO spot test.



Spot checker (Complete set of included items)



Left: evaluation 1, good compatibility Right: evaluation 5, very poor compatibility

# How to use

The outline of manual and judgment of "Spot checker" is as shown in the following figure and flow chart. As the obtained number of evaluation is 3 or higher, compatibility (stability) is judged to be not good.

In such cases, it may cause problems such as sludge formation.

(The higher number, the amount of sludge actually formed increases exponentially)

Evaluation	Comments	Countermeasures
1~2	Compatibility (stability) is good.	—
3~6	Compatibility (stability) is not good.	Enhanced monitoring of FO strainers and
	Possibility of sludge trouble.	Consider to dose "Yunic 800VLS" for VLSFO.

## Spot checker <Simple instruction manual for compatibility of marine fuel oil > () NIPPON YUKA KOGYO

H-1	Glass beaker
H-2	Stirring Rod
H-3	Hot Plate
H-4	Filter Paper
H-5	Punching Plate
H-6	Reagent
H-7	Belo-Pet
H-8	Forcep
J-5	Thermometer



(1) Collect FO samples Delivered Storaged 15mL 15mL Prepare 30mL of Mixed FO Parts to use: H-1, H-2	<ul> <li>(2) Prepare Hot plate</li> <li>⇒ Warm up mixed FO</li> <li>⇒ Dry up Filter Paper</li> <li>✓</li> <li>✓</li></ul>	(3) Carry out "FO Spot ⇒ 1 drop for each filter After stirring well with a s 1 drop on the center of Parts to use: (H-3 H-5), H-2	paper Goo Not g
<ul> <li>Only delivered if test FO alone</li> <li>(4) Dry FO on Filter Paper</li> <li>⇒ Dry FO by Hot plate</li> <li>Not dryed</li> </ul>	Use Hot Plate in combination with Punching Plate.	Surface is very HOT.	Evaluation 2
Dryed well Wait at least 5 minutes	To evaluate, refer the documents	Evaluation 3	
Parts to use: (H-3 H-5)	1. "Evaluation standard sheet"	⊒≓ (0, 3	17 (A 4
Surface is very HOT.	2. "Reference photos for fuel oil spot te	st evaluation"	5 Evaluation 6

- Please refer to the "Instruction manual booklet " for other detailed operation and so on. - Please contact NIPPON YUKA KOGYO for questions about how to operate or evaluate. HEAD OFFICE : E-mail sales-one@nipponyuka.com, KOBE OFFICE : E-mail yukakb@nipponyuka.com

valuation 1	Evaluation 2		状態	試料油を滴下したところにリング(内円)が全く認められない
		評価1		説特通を洞下したとこうにリンク(内口)が主く認められない。 There is no inner circle.
	Good	##1回1 Evaluation1	Appearance コメント	There is no inner circle. 安定性に問題ありません
		Evaluation		
			Comment	Compatibility (Stability) is Good.
			状態	周囲が不完全な内円が僅かに認められる
	and the second se	評価2	Appearance	Inner circle color is unclear.
評価1	22 (11) (11) (11) (11) (11) (11) (11) (1	Evaluation2	コメント	安定性に問題ありません
			Comment	Compatibility (Stability) is no problem.
aluation 3	Evaluation 4			
	The second se		状態	周囲が完全な線上の内円が認められ、内円と外円の色はほとんど同じである
ALC: NO	and the second sec	評価3	Appearance	Inner circle color is same as outer circle.
	0	Evaluation3	コメント	安定性がやや悪く、スラッジトラブルが発生する可能性が有ります
			Comment	Compatibility (Stability) is slightly bad and this fuel oil has possibility that the sludge trouble may occur
			状態	内円の縁が黒色になり、内円内部の色は外円より濃くなる
A MARKEN AND A MARKAN	And a second	評価4	Appearance	Inner circle color in darker compared to outer circle color.
評価3	評価4	Evaluation4	コメント	安定性がやや悪く、スラッジトラブルが発生する可能性が有ります
at 142 O	5T 161 14		Comment	Compatibility (Stability) is slightly bad and this fuel oil has possibility that the sludge trouble may occu
aluation 5	Evaluation 6			
1.14			状態	内円内部はさらに濃くなり、中心付近以外はほぼ黒色になる
	and the second s	評価5	Appearance	Inner circle color is almost black
0		Evaluation5	コメント	安定性が悪く、スラッジトラブルが発生する可能性が高いです
			Comment	Compatibility (Stability) is bad and this fuel oil has high possibility that sludge trouble will occur.
			1	
Property in the second			状態	内円が完全な黒色となり、僅かに盛り上がった状態となる
	Bad	評価6	Appearance	Inner circle color is single color of black and it get thicker.
評価 5	評価6	Evaluation6	コメント	安定性が悪く、スラッジトラブルが発生する可能性が高いです
			Comment	Compatibility (Stability) is bad and this fuel oil has high possibility that sludge trouble will occur.
		評価1~2		安定性に問題なし
	重油のスポット評価			

Evaluation (standard) sheet for spot test.

Good Compatibility (Stability) トラブル発生の可能性あり Abnormal (There is a possibility of sludge trouble)

# NIPPON YUKA KOGYO CO.,LTD.

HEAD OFFICE : 3-9, KAIGAN-DORI, NAKA-KU, YOKOHAMA, 231-0002, JAPAN Tel+81-45-201-8867 FAX. +81-45-201-8358 KOBE OFFICE : 1-1-1, KAIGAN-DORI, CHUO-KU, KOBE, 650-0024, JAPAN

評価3~6

Evaluation  $3 \sim 6$ 

TeL+81-78-321-4105 FAX. +81-78-321-4107



# Yunic 750LS-F

A lubricity improver and microbial inhibitor for low-sulfur gas oil and heavy oil (bunker A)



# $(\gamma)$

NIPPON YUKA KOGYO CO.,LTD.

Head Office Yusen Building 3F, 3-9 Kaigandori, Nakaku, Yokohama 231-0002, Japan TEL: 045-201-8867 FAX: 045-201-8358

Kobe Sales Office Kobe Yusen Building 1F, 1-1-1 Kaigandori, Chuoku, Kobe 650-0024, Japan TEL: 078-321-4105 FAX: 078-321-4107 This document, and more, is available for download from Martin's Marine Engineering Page - www.dieselduck.net

# **Product details**

# Characteristics

- Appearance: light yellow to light brown transparent liquid Density: 870~910 kg/m at 15°C
  - Flash point: 67 °C (PM closed cup tester)
- Main components : fatty acids, nitrogen compounds, petroleum solvents

# **Properties**

Yunic 750LS-F is an additive for low-sulfur gas oil and heavy oil (bunker A) that prevents problems due to poor lubricity and fungal growth. Its properties and effects are described below.

Improved Lubricity

The lubricity of fuel oil is improved by Yunic 750LS-F. As evaluated by the high-frequency reciprocating rig (HFRR) test, which is one index of lubricity, the low lubricity of low-sulfur diesel oil with a wear scar diameter of approximately 600  $\mu$  m reduce to 460  $\mu$  m or less in line with engine manufacturer recommendations. Note: A smaller wear scar diameter in the HFRR test have a better lubricity.

Microbial sludge suppression

Yunic 750LS-F gives fuel oil fungicidal properties. This provides a preventive effect over the long-term and it also prevents the growth of any fungus already present.

# Method of use

- The standard additive rate of Yunic 750LS-F is 1/2500 when the sulfur content of the fuel oil is 0.1% (m/m) or less.
- Yunic750LS-F mixes well with fuel oil. However, mixing is further promoted by feeding Yunic750LS-F into the fuel oil storage tank before supplying the oil.

# Precautions for use

- Flammable. No open flames.
- Wear protective equipment such as goggles, a mask, and oil-resistant gloves.
- First aid measures
  - In the event of eye contact, immediately flush with plenty of water for at least 15 minutes.
  - In the event of skin contact, wash well with soapy water and apply skin cream.
  - In the event of vapor inhalation, move to a well-ventilated area and keep the body warm.
  - \* Seek medical treatment as necessary.

# Storage precautions

- No fire
- Store in a cool, dark place
  - Do not store at 50 °C or above or below 0 °C. The product may partially freeze when stored near 0°C. If partial freezing occurs, return the product to room temperature before use.

# Packing

●200 L drum ●18 L oil can

• Weight : 198.7kg Weight : 17.2kg

• Dimensions :  $\varphi$  58.5cm  $\times$  89cm

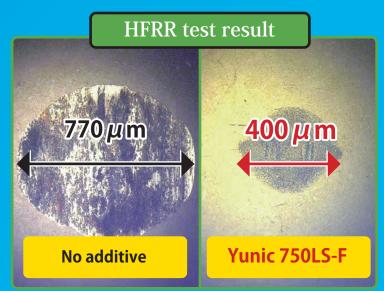
• Dimensions (W  $\times$  D  $\times$  H): 23.8cm  $\times$  23.8cm  $\times$  35cm

# Yunic 750LS-F

# A hybrid-performance additive that improves lubricity and suppresses fungal sludge.

# **Improved lubricity**

The lubricity of fuel oil generally correlates with its kinematic viscosity and sulfur content. The high-frequency reciprocating rig (HFRR), which measures wear on a test steel ball, which is used to evaluate the lubricity of fuel oil. When the lubricity improver Yunic 750 LS-F being added at the standard addition rate of 1/2500 to LSGOs supplied at an external location, it was possible to reduce the HFRR scar diameter for all LSGOs and also able to meet the standard for land use (460  $\mu$  m or less), which is more stringent than the one used for marine standard.



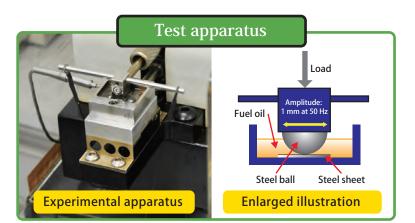
# **Overview of the high-frequency reciprocating rig (HFRR) test**

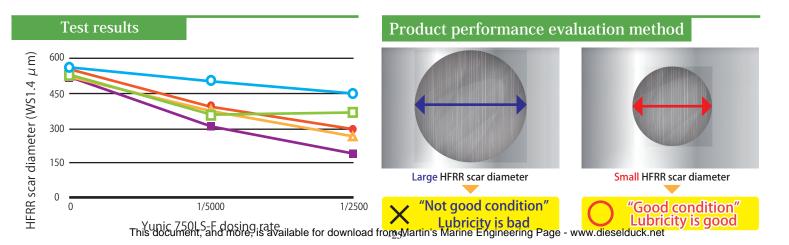
## HFRR test standards

#### Maritime

- →Marine fuel oil standard ISO 8217 (2012 version) DMA or DMB HFRR scar diameter: 520  $\mu$  m or less ●Land
  - →EN 590 (European diesel standard), ISO 12156-2 Gas oil HFRR scar diameter: 460  $\mu$  m or less

According to recent HFRR test results for LSGO procured from overseas, the proportion of LSGO not conforming to maritime and land standards was about 3% and 8%, respectively.



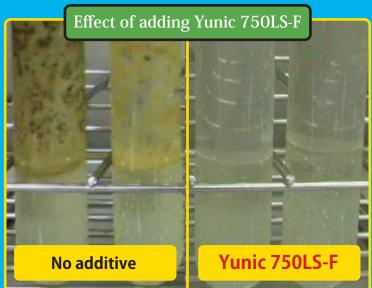


# A lubricity improver and fungal inhibitor for low-sulfur gas oil and heavy oil (bunker A)

Since January 1, 2015, most of the fuel oil used in emission control areas (ECAs) has been switched from conventional low-sulfur fuel oil (LSFO) to low-sulfur gas oil (LSGO) with a sulfur content of 0.1% or less and low-sulfur diesel oil (LSDO). Also, the decision has been made to limit the sulfur content in the marine fuel oils used in all marine areas outside ECAs to 0.50% or less from January 1, 2020, and it is anticipated that the use of LSGO and LSDO will further increase. The lubricity of LSGO and LSDO is generally low, leading to concerns that various new problems may arise due to the deterioration in lubrication. In addition, because fuel oil tanks in which LSGO and LSDO are stored and not heated, there is the possibility of fungal growth in the oil due to factors such as condensation water. Dosing Yunic 750LS-F to LSGO and LSDO contributes the following effects.

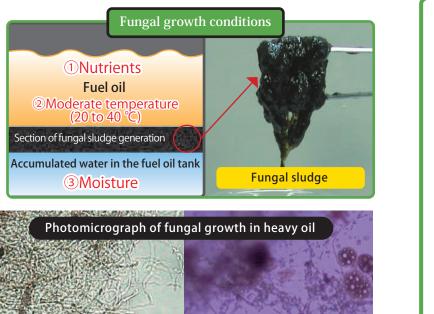
# **Fungal sludge suppression**

Fungal spores that enter the fuel oil tank make use of the fuel oil as a source of nutrients and multiply to form a thick sludge. Fungal growth in the fuel oil causes the strainer being blocked, potentially leading to serious engine trouble such as blackouts. When Yunic 750 LS-F is added, fungal growth is suppressed. Fungal filaments are gradually broken down, and clogging of the strainer/pipeline can be prevented, along with the accumulation of fungal sludge in the fuel tank.



# Causes of fungal sludge

Fungal growth can occur in fuel oil when fungal spores are mixed into a fuel oil tank that has suitable conditions for growth, namely, nutrients, moisture, and a moderate temperature. When these conditions are met, growth occurs at the interface between the fuel oil and water. Low-sulfur gas oil and heavy oil (bunker A) has a low viscosity and further not being heated in the fuel tank, making t/hem the ideal fungal growth environment.



# Patent and Certificate

Yunic 750 LS-F got a patent in August 2018. (Patent No. 6371687, entitled "Composition for Improving fungal growth suppression and Lubricity of fuel oil") In addition, it was confirmed that the Lubricity of fuel oil are improved by addition of Yunic 750LS-F to the LSGO used in the investigation, and a certificate (Statement of Fact) has been obtained from Nippon Kaiji Kyokai (Class NK).

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Doing rate         additive         1:500         1/2300           Tot field olds         Ware sear dumented WED by HPRR test jumit         1:500         1:500           5500 h         700         450         400           15500 m         710         400         400           * 11500 means Low Solpher Gas Oll.         710         400         400           ** 11500 means Low Solpher Gas Oll.         710         400         400           ** 1150 means High Trespress Receiverating Big.         Advort memioned inspection test results are confirmed in accordance with test procedure and advort memioned inspection test results are confirmed in social wate of the search proceedure of the search proceedure was changed due to	Doing rate         additive         1:500         1/2300           Tot field olds         Ware sear dumented WED by HPRR test jumit         1:500         1:500           5500 h         700         450         400           15500 m         710         400         400           * 11500 means Low Solpher Gas Oll.         710         400         400           ** 11500 means Low Solpher Gas Oll.         710         400         400           ** 1150 means High Trespress Receiverating Big.         Advort memioned inspection test results are confirmed in accordance with test procedure and advort memioned inspection test results are confirmed in social wate of the search proceedure of the search proceedure was changed due to			NIS. Refer to and	cneu report of gene	rat properties of tes	tines ous
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LSG0 A         720         450         400           LSG0 B         640         640         450           * LSG0 Care Leve Solphar CarcOL         710         470         450           * "UHR3 " means High Troponcy Reciprocating Rig.         7         200         7         200           * Common High Troponcy Reciprocating Rig.         7         8         200         7         200           * difference mensioned inspection toir strailus are confineed in accordance with test procedure and mechan.         6         7         200         400         100 <td< td=""><td>LSG0 A         720         450         400           LSG0 B         640         640         450           * LSG0 Care Leve Solphar CarcOL         710         470         450           * "UHR3 " means High Troponcy Reciprocating Rig.         7         200         7         200           * Common High Troponcy Reciprocating Rig.         7         8         200         7         200           * difference mensioned inspection toir strailus are confineed in accordance with test procedure and mechan.         6         7         200         400         100         <td< td=""><td></td><td>Test fuel oils</td><td>Wear scor di</td><td>ameter(WSD) by H</td><td>FRR test [um]</td><td></td></td<></td></td<>	LSG0 A         720         450         400           LSG0 B         640         640         450           * LSG0 Care Leve Solphar CarcOL         710         470         450           * "UHR3 " means High Troponcy Reciprocating Rig.         7         200         7         200           * Common High Troponcy Reciprocating Rig.         7         8         200         7         200           * difference mensioned inspection toir strailus are confineed in accordance with test procedure and mechan.         6         7         200         400         100 <td< td=""><td></td><td>Test fuel oils</td><td>Wear scor di</td><td>ameter(WSD) by H</td><td>FRR test [um]</td><td></td></td<>		Test fuel oils	Wear scor di	ameter(WSD) by H	FRR test [um]	
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This document, and more, is available for download fromd Martin's Marine Engineering Page - www.dieselduck.net

# Attachment 3

# Documents provided by Ichinen Chemicals Co., Ltd

Effective method and product for dispersion and removal of sludge accumulated in storage tank of HSFO use ship – Fuel additives for tank cleaning – EXCLEAN RS, TAICRUSH A-38

Effective methods and products for preventing and solving sludge generation by mixing HSFO and 2020 SOx regulatory fuel oil (VLSFO) – Sludge suppressant / dispersant fuel additives – TAICRUSH A-38 / TAICRUSH VL-20

Effective methods and products for preventing and solving problems with 2020 regulatory fuel oils – Variety of fuel additives

Procedure, method and product for spot test – Spot test kit

Sludge suppressant and dispersant for 2020 SOx regulatory FO – TAICRUSH VL-20

Effective method and product for dispersion and removal of sludge accumulated in storage tank of HSFO use ship Fuel additives for tank cleaning <EXTCLEAN RS. TAICRUSH A-38> Inchinen Chemicals Co. Ltd.

Yasuhiro Ichimura

Takehiro Ishiwatari Kaikou Hirabayashi Natsuro Kuboi Satoshi Ozaki

#### 1. Introduction

From January 1, 2020, the marine fuel oil sulfur emission regulations in the MARPOL Annex will be strengthened from 3.5% to 0.5%.

Measures against this sulfur emission include alternative fuels (LNG, etc.), SOx scrubber loading, and 2020 regulatory fuel oils.

This paper introduces methods and products that use fuel additives for tank cleaning, which is recommended as a preliminary preparation for the use of 2020 regulatory fuel oils.

#### 2. Fuel additives

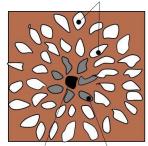
#### 2.1 Asphaltenic sludge

Asphaltenes are polycyclic aromatic hydrocarbons that are insoluble in n-heptane and soluble in benzene, and are black-brown solids containing elements such as nitrogen, oxygen, and sulfur.

Asphaltene adsorbs a resin called marten, which forms micelles and is dispersed stably in oil (Fig. 1).

However, asphaltene begins to agglomerate when the micelle balance is lost due to factors such as dissolving power, temperature change, and pressure change, and eventually agglomerates into large particles (Fig. 2), which is called asphaltenic sludge.

Marten



Carboid Asphaltene

Fig1.Asphaltene in oil

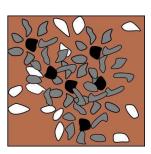


Fig2. Asphaltene during agglomeration

#### 2.2 Types of fuel additives

We have two types of fuel additives for tank cleaning. One is a sludge solubilizer that acts on asphaltenic sludge and dissolves asphaltenes to reduce the sludge content. Another is a sludge dispersant that suppresses asphaltenic sludge precipitation in C heavy oil.

Application	Product name
Asphaltenic sludge solubilizer	EXTCLEAN RS
Asphaltenic suppressant and	
dispersant of sludge	TAICRUSH A-38
precipitation	

#### 3. Sludge solubilizer (EXTCLEAN RS) 3.1 Application

It is recommended to clean the inside of the FO tank and remove the accumulated sludge as a preliminary preparation when refilling the ship with 2020 regulatory fuel oil.

However, tank cleaning work is difficult to implement due to manual cleaning costs and restrictions such as suspension of operation during the working period.

We have developed a sludge solubilizer that has the following performance and exhibits a tank cleaning effect.

#### 3.2 Performance

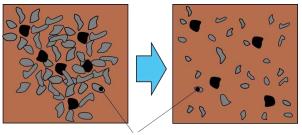
- Rapid sludge dissolution
- 2 No negative impact on the engine mechanism
- ③ Combustible with fuel oil
- ④ Can be stored on the ship

The action of EXTCLEAN RS on asphaltenic sludge utilizes the property that the main component, petroleum hydrocarbons, dissolves asphaltenes in the sludge. This product is a petroleum-based product that can be mixed with fuel and consumed on board, and no landing or incineration is required. The flash point does not fall under the flammable liquids of the Ship Safety Act and can be stored on the ship.

Classification:	Oiliness		
Appearance:	Transparent liquid		
Specific gravity:	0.89 (at 20°C)		
Flash point:	65°C		
Main	Petroleum hydrocarbons		
component:			

#### 3.3 Sludge dissolution performance

Asphaltene sludge has the property of being easily precipitation, causing problems such as accumulation on the tank bottom and strainer clogging. EXTCLEAN RS contains a component that dissolves asphaltenic sludge and exerts a dissolution effect on sludge that has alreadyprecipitated and deposited (Fig. 3).



Asphaltene

Fig 3. Dissolution of asphaltenic sludge

#### 3.4 FO Tank cleaning using EXTCLEAN RS

During tank cleaning, the environment and conditions for the use of additives are diverse, such as the hull shape, tank shape, and tank internal state (sludge accumulation amount). It is recommended to check the FO tank status before decision of the tank cleaning method.

- 1 Drain the fuel oil in the tank as much as possible.
- ② Add up to 10% of EXCLEAN RS to the residual fuel and keep it for about 1 to 2 weeks to dissolve sludge. \* 1
- ③ With bunkering (shifted) add up to the fuel tank, and the softened and dissolved sludge is dispersed in the fuel oil.
- ④ Cleaning completed \* 2

\* 1 When the vessel is swayed in voyage, EXCLEAN RS and sludge components are mixed, and softening and dissolution progress.

\* 2 EXCLEAN RS can be used as fuel, and fuel oil after washing is consumed quickly.In order to prevent sludge reprecipitation, it is recommended to use sludge dispersant fuel additives.

### 3.5 Performance test of EXTCLEAN RS 3.5.1 Solubility of EXTCLEAN RS pseudo sludge

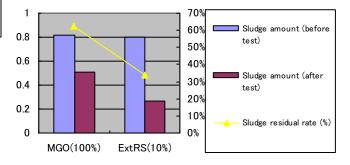


Fig.4. Pseudo sludge dissolution performance test results with MGO alone and EXTCLEAN RS mixed fuel (in-house test)

Contaminants in HSFO were spun down to extract pseudo sludge and used as a test sample.

MGO alone and MGO containing 10% EXTCLEAN RS were prepared, and the pseudo sludge was swayed in the solvent. After swing, 60mesh filtration was performed, and the dissolution performance of the pseudo sludge was evaluated and confirmed.

As a result, the fuel with EXTCLEAN RS added showed higher sludge dissolution performance than MGO alone (Figs. 4 and 5).





Fig 5. 60mesh filtration residue Left: MGO alone Right: ExtRS (10%)

In addition, when carrying out ship tank cleaning, it can be expected to prevent re-precipitation / sedimentation of dissolved sludge by using it together with sludge dispersant fuel additives.

#### 3.5.2 Test engine strainer cleaning effect

The test engine was operated with 10% EXTCLEAN RS added to the HSFO, and the strainer state was observed after the operation with and without the addition of EXTCLEAN RS (Fig. 6).



Fig 6. Test engine strainer condition Left: ExtRS not added Right: ExtRS 10% added

#### Sludge precipitation suppressant / dispersant (TAICRUSH A-38)

#### 4.1 Tank cleaning with sludge dispersant

Sludge dispersant is an additive that acts to dispersion and suppress of aggregation for sludge in fuel oil.

After adding TAICRUSH A-38, our sludge dispersant, to the tank, it is mixed and agitated by refueling to obtain a sludge sedimentation suppressing effect. Aggregation and sedimentation of sludge is suppressed by the dispersant, contributing to tank cleaning.

- ①Add TAICRUSH A-38 to the FO tank before bunkering.
- ②Repeat the dosage 3 times before bunkering (Table 3).
- ③Cleaning completed.

Table 3. TAICRUSH A-38 tank cleaning fuel additive amount

(example)				
	Recommended dosing amount for tank			
Dosing	cleaning			
times	Dosage	A-38(L)	Fuel oil(MT)	
	rate	A-30(L)		
1 <sup>st</sup>	1/8000	1	8	
2 <sup>nd</sup>	1/8000	1	8	
3 <sup>rd</sup>	1/5000	1	5	

#### 4.2 How to use additives

Before bunkering, add the recommended amount of fuel additives from the air vent or sounding pipe. In order to effectively infiltrate the chemical into the sludge accumulated at the bottom of the tank, add the additive with the tank residual oil drained as much as possible, and physically mix and agitate with the pulsation at the time of bunkering.

#### 5. Conclusion

Although tank cleaning is recommended as a preliminary preparation for the introduction of 2020 regulatory fuel oils, it is difficult to do so due to manual tank cleaning costs and operational suspension during the cleaning period.

EXTCLEAN RS, a fuel additive for tank cleaning developed by our company, has sludge solubility and can be cleaned in a short period of time during operation.

In the future, even in the process of launching regulatory-compliant oils into the market and supplying fuels with various oil properties, we will continue research and development from a broad perspective to promote the safe operation of ships and the improvement of economic efficiency.

Contact Details Ichinen Chemicals Co., Ltd Kobe Sales Office TEL: +81 78-231-1024 FAX: +81 78-231-1030 E-mail osaka@ichinen-chem.co.jp Tokyo Sales Office TEL: +81 3-6414-5609 FAX + 81 3-6414-5621 E-mail tcsecond@ichinen-chem.co.jp Effective methods and products for preventing and solving sludge generation by mixing HSFO and 2020 SOx regulatory fuel oil (VLSFO) Sludge suppressant / dispersant fuel additives [TAICRUSH A-38/ TAICRUSH VL-20] Ichinen Chemicals Co., Ltd.

Yasuhiro Ichimura Takehiro Ishiwatari

Natsuro Kuboi Satoshi Ozaki

Kaikou Hirabayashi

## 1. Introduction

From January 1, 2020, the MARPOL Convention Annex IV will implement a reduction from the upper limit of 3.5% to 0.5% for the limit of sulfur emissions from marine fuel oil in general sea areas. Although SOx and PM are expected to be reduced by reducing the sulfur content of marine fuels, the diversification of properties is expected depending on the properties of crude oil, refinery-specific manufacturing methods, fuel oil blending methods, etc.

Regulated oils after 2020 are expected to be supplied with paraffinic fuel in addition to polycyclic aromatic fuel, which has been the mainstream, due to diversification of properties. Therefore, there is a concern that when both fuels are mixed, the stability is impaired and the possibility of asphaltic sludge generation increases.

This article introduces sludge suppressant / dispersant fuel additives that are effective in suppressing asphaltene sludge precipitation that is a concern in case of mixing fuels or mixing regulatory compliant oils when switching from conventional fuel (HSFO) to regulated oil (VLSFO/Very Low Sulfur Fuel Oil).

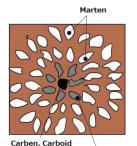
# 2. Sludge suppressant/ dispersant fuel additives [TAICRUSH series]

## 2.1 Asphaltenic sludge

Asphaltenes are polycyclic aromatic hydrocarbons that are insoluble in n-heptane and soluble in benzene, and are black-brown solids containing elements such as nitrogen, oxygen, and sulfur.

Asphaltene adsorbs a resin called marten, which forms micelles and is dispersed stably in oil (Fig. 1).

However, asphaltene begins to agglomerate when the micelle balance is lost due to factors such as dissolving power, temperature change, and pressure change, eventually becoming large particles (Fig. 2). This is called asphaltenic sludge.



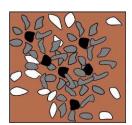


Fig.1. Asphaltene in oil.

Fig. 2. Asphaltene during agglomeration.

## 2.2 Causes of asphaltenic sludge troubles <Compatibility (mixing stability) problem>

Asphaltene

When light oil is added to heavy oil, the marten content is dissolved and the protection of the surface layer may be lost. Since the exposed asphaltenes and carbides have polarity, they bond together to form a huge asphaltenic sludge.

## <Thermal stability problem>

When heat is applied to stable fuel oil, factors such as dissolution of the micelle surface layer, decrease in viscosity (decrease in suspension force), and thermal motion of particles, it is thought that precipitation of asphaltenic sludge is promoted.

## <Storage stability problem>

Oxidation degradation due to oxygen in the air and heavy fuel segregation and sedimentation occur over time during fuel storage.

#### 2.3 Sludge suppressant / dispersant fuel additives

We are developing products that respond to various concerns in order to use marine fuel safely and economically, whose properties are very much diversifying.

Here, we introduce products developed using our knowledge of sludge suppression / dispersion performance over many years for 2020 regulatory fuel oil (VLSFO).

Table 1. Examples of our sludge suppressant / dispersant.

Effects	Product name
Sludge suppressant / dispersant with combustion accelerator.	TAICRUSH A-38
[Newly developed] Sludge suppressant / dispersant for 2020 regulatory fuel oil.	TAICRUSH VL-20

TAICRUSH VL-20 was developed as a fuel additive that suppresses sludge precipitation due to sludge troubles, which is a concern when using VLSFO residual oil grade (RM: Residual Marine Fuel) compliant with SOx emission regulations from 2020 It is a product.

This product is effective in preventing sludge troubles caused by the unique properties of 2020 regulatory fuel oils (VLSFO) by strengthening sludge suppressant with new ingredients. Also, by dispersing sludge in the fuel oil in a fine state, it contributes to cleaning the F.O tank, strainer, cleaner, piping, etc. This product also exhibits sludge suppression effect against HSFO used on SOx scrubber equipped ships.

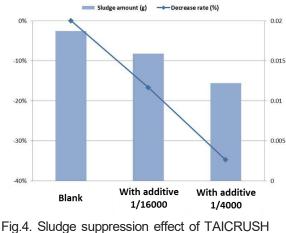
#### 2.4 Performance test

The sludge suppression effect was verified using 2020 regulatory fuel oil. Regulatory fuel oil with TAICRUSH VL-20 dosed (1/16000) and non-dosed regulatory oil were added to the colorimetric tube and dispersed in n-heptane, confirming the precipitation of asphaltenic sludge (Fig. 3). As the marten covering the asphaltenes is soluble in n-heptane, aggregation of asphaltenes is promoted in heptane. In addition, in an

in-house test based on the Japan Shipowners Association dispersion test, the sample with TAICRUSH VL-20 dosed showed a sludge suppression effect of about 16 to 35% depending on the amount dosed, compared with the non-dosed sample (Fig. 4).



Fig. 3.Dispersion test with n-heptane.



VL-20 against VLSFO alone.

#### 2.5 How to use

By using TAICRUSH VL-20 in combination with our fuel spot test kit, the optimum addition rate can be selected for each 2020 regulatory fuel oil. This can improve the economics of chemicals. The standard dosage amount of TAICRUSH VL-20 is 1/16000. If it is judged that there is a concern about fuel compatibility (mixing stability) / single stability using a test kit, it is recommended to use it after adjusting the dosage rate. Sampling the bunker fuel, residual oil, etc. in the ship's fuel tank, mixed oil, and conduct spot test with a test kit. After the test, adjust the dosage rate of TAICRUSH VL-20 according to the Reference Spot No. (Fig. 5).

ASTM D 4740	Reference Splot	Spot Description	TAICRUSH VL-20
No. 1		Homogeneous spot, no inner ring	1
No.2		Paint or poorly defined inner ring	Add to 1/16000~10000
No.3		Well-defined inner ring, only slightly darker than the background	
No. 4	0	Well-defined inner ring. thicker than the ring is reference spot ro.3 and somewhat darier than the background	_ Add to 1/5000~2500
No.5	•	Very dark solid or nearly solid area in the center, the central area is much darker than the background	

Fig.5. Fuel spot test kit (TAICRUSH VL-20 reference dosage rate) \*

\* The dosage rate was created based on the internal test of Ichinen Chemicals.

The content may be updated depending on the properties of the compliant oil to be supplied.

Table 2. Properties of TAICRUSH VL-20.

Classification	Oiliness
Appearance	Light yellow transparent liquid
Specific gravity	0.92 (at 20°C)
Viscosity	50 mPa•s (at 20°C)
Flash point	65°C

## 3. Conclusion

This report describes sludge problems and our products for preventing and solving them.

2020 regulatory fuel oils are expected to have more diversified properties than before, and there is concern about poor mixing stability (compatibility). Asphaltic sludge is feared even in 2020 regulatory fuel oils, but it is effective to use a sludge dispersant to avoid sludge problems. We have developed a new sludge dispersant, TAICRUSH VL-20, in anticipation of stricter SOx regulations beginning in 2020. In the future, the introduction of regulatory compliant oils will begin, and in the process of supplying fuels with various oil properties, we intend to continue research and development from a broad perspective so that we can contribute to the safe operation and economic efficiency of ships. Contact Details Ichinen Chemicals Co., Ltd Kobe Sales Office TEL: +81 78-231-1024 FAX: +81 78-231-1030 E-mail osaka@ichinen-chem.co.jp Tokyo Sales Office TEL: +81 3-6414-5609 FAX + 81 3-6414-5621 E-mail tcsecond@ichinen-chem.co.jp

# Effective methods and products for preventing and solving problems with 2020regulatory fuel oils Variety of fuel additives Ichinen Chemicals Co., Ltd.

Yasuhiro Ichimura Takehiro Ishiwatari Kaikou Hirabayashi Natsuro Kuboi Satoshi Ozaki

## 1. Fuel additives

Sulfur content in marine fuel oil is reduced from 3.5% to 0.5% due to stricter environmental regulations. As a result, diversification of fuel oil production methods and fuel oil properties is expected, and there is a concern that problems may occur in various mechanisms of the engine due to fuel properties that did not exist before. For example, problems such as sludge precipitation due to poor mixing stability (compatibility) and paraffin wax precipitation from low-sulfur base materials may occur.

This section introduces fuel additives that have an improvement effect on various concerns after the introduction of 2020 regulatory fuel oil.

Table 1. Problems and Concerns by 2020 regulatory fuel oil properties

Problems	Concerns
Compatibility / single stability	Asphaltene / wax properties
Compatibility / single stability	sludge precipitation
Low kinematic viscosity	Abnormal wear of fuel
	injection system equipment
Low temperature fluidity	Paraffin wax precipitation
Ignition / combustibility	Ignition / combustibility
	deterioration

#### Table 2. Fuel additives by application

Application	Fuel additives
Asphaltene sludge	
Precipitation suppressant/	TAICRUSH VL-20
dispersant	
Lubricity improver/ antimold	LUB-UP HS
agent	
Pour point improver	TAICRUSH PPC
Combustion accelerator	TAICRUSH LC

### 2. Asphaltene sludge precipitation suppressant / dispersant TAICRUSH VL-20

## 2.1 Application

Asphaltene sludge precipitation suppression and dispersion.

#### 2.2 Effect

Suppresses sludge precipitation due to poor storage and mixing stability, which is a concern when using the residue grade RM (Residual Marine Fuel) of VLSFO (Very Low Sulfur Fuel Oil).

## 2.3 How to use

Standard dosage 1/16000

Check the fuel mixing stability (compatibility) / single stability using our test kit. If there is a concern about stability, adjust the dosage rate and use it.

Table 3. Properties of TAICRUSH VL-20

Classification:	Oiliness
Appearance	Light yellow transparent liquid
Specific gravity:	0.92 (at 20°C)
Viscosity:	50 mPa ⋅ s (at 20°C)
Flash point:	65°C

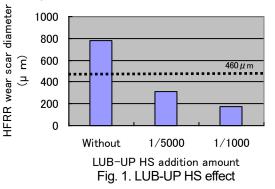
## 3. Lubricity improver/ antimold agent LUB-UP HS

#### 3.1 Application

#### 3.2 Effect

Prevents abnormal wear and sticking of the fuel supply system due to a decrease in lubricity, which is a concern with low sulfur and low kinematic viscosity fuels, and blockage in the fuel supply path due to mold mycelium.

When the HFRR test was performed using a sample with 1/5000 of LUB-UP HS, the wear scar diameter was less than 460  $\mu$ m (ISO12156-2), and the lubricity was improved.



Improvement of lubricity and mold growth prevention of low-lubricity fuel.

#### 3.3 How to use

Standard dosage 1/5000

Table 4. Properties of LUB-UP HS	
Classification:	Oiliness
Appearance:	Yellow transparent liquid
0 10 11	a = a + (a + a + a) = b

Specific gravity:	0.96 (at 20°C)
Viscosity:	320 mPa ⋅ s (at 20°C)
Flash point:	>100°C

## 4. Pour point improver TAICRUSH PPC

## 4.1 Application

Improved low-temperature fluidity of distillate oil

#### 4.2 Effect

By adding a small amount to the distillate fuel oil, PP (pour point) and CFPP (cold filtration clogging point) are reduced (Figs. 2 and 3), prevents fuel oil solidification in fuel tanks and fuel systems at low temperatures.

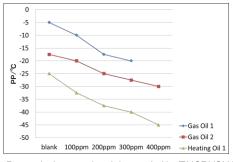


Fig.2. Pour point improved and descended by TAICRUSH PPC

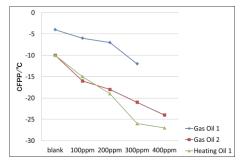


Fig.3. Low temperature clogging point was improved and dropped by TAICRUSH PPC

#### 4.3 How to use

Standard dosage 1/2000

Mixing and agitation is promoted by supplying the required amount of TAICRUSH PPC to the fuel tank before bunkering.

Even if dosed to already solidified fuel oil, fluidity cannot be recovered, so add it before solidifying.

Table 5. Properties of TAICRUSH PPC

Classification:	Oiliness
Appearance:	White to yellow liquid
Specific gravity:	0.92 g/cm <sup>3</sup> (at 40°C)
Viscosity:	24 mm²(at 100°C)
Flash point:	63°C

## 5. Combustion accelerator TAICRUSH LC

5.1 Application

Fuel oil combustion accelerator

## 5.2 Effect

It exerts a combustion accelerating effect on fuel oil that has deteriorated in combustibility due to an increase in the ratio of aromatic components, and it reduces unburned components and suppresses the formation of deposits on the fuel valve, piston ring, combustion chamber, and exhaust system.

#### 5.3 How to use

Standard dosage 1/6000

This product is a liquid type, and the appropriate amount is put directly into the F.O tank or injected into the line.

Table 6 Drapartian of TAICDUCU I

Classification:	Oiliness
Appearance:	Brown transparent liquid
Specific gravity:	0.91 (at 20°C)
Viscosity:	<10 mPa ⋅ s (at 20°C)
Flash point:	65°C

Contact Details Ichinen Chemicals Co., Ltd Kobe Sales Office TEL: +81 78-231-1024 FAX: +81 78-231-1030 E-mail osaka@ichinen-chem.co.jp Tokyo Sales Office TEL: +81 3-6414-5609 FAX + 81 3-6414-5621 E-mail tcsecond@ichinen-chem.co.jp

## Procedure, method and product for spot test Spot test kit Ichinen Chemicals Co., Ltd.

Yasuhiro Ichimura

Takehiro Ishiwatari Kaikou Hirabayashi Natsuro Kuboi Satoshi Ozaki

## 1. Spot test

The spot test evaluates the single stability and mixing stability (compatibility) of the fuel oil according to the state of the spot generated by dropping the fuel oil on the filter paper.

The spot test has the following characteristics:

• Simple fuel stability test

• Predict the likelihood of failure depending on the degree and amount of sludge.

We will introduce the usage and products of the spot test kit that we handle as one of the indicators to improve the mixing stability (compatibility) of fuel oil, which is a concern of 2020 compliant fuel oils.

## 2. Spot test kit (Product example) (Compatibility and Stability Test Kit)



Fig.1. Product appearance

## 2.2 How to use

Fuel oil on board (A), bunker fuel (B). Prepare mixed oil (A + B) and conduct a spot test.

Check the amount of fuel oil in the ship's tank and supplementary and determine the mixing ratio.

## 2.3 Compatibility and stability test method

① Pour about 30ml of water into the main body heating cylinder.

Be sure to Pour water to prevent heating of the test kit body and damage to the glass tube.

- (2) Add 50 ml of fuel oil to the glass tube to check the stability of the single fuel.
   When checking the compatibility, add 50 ml each of fuel oil (A) and fuel oil (B) to the glass tube.
- ③ Set a thermometer into the glass tube (the thermometer also serves as a stirring bar).
- ④ Turn on the power switch of the test kit. The temperature starts rising to the set temperature recorded on the main unit. The set temperature in this test is 95 ° C.
- (5) Using a thermometer, stir the sample, raise the temperature to 95 ° C, and hold for 15 to 20 minutes.
- (6) Install a filter paper on the glass petri dish and remove thermometer from the glass tube. Do not apply the first drop of oil drops from the removed thermometer. And drop the second drop on the filter paper.
- ⑦ Dry the filter paper at 100 ° C for 60 minutes. (Use oven or hot plate)
- (8) Judge the Reference Spot No. from the spot ring of the filter paper and determine the dosing amount of TAICRUSH VL-20.

%Please contact us for the specifications of our products.2.4 Judgment of spot ring

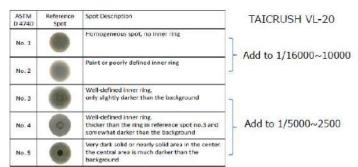


Fig. 2. Reference Spot No.

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# TAICRUSH VL-20

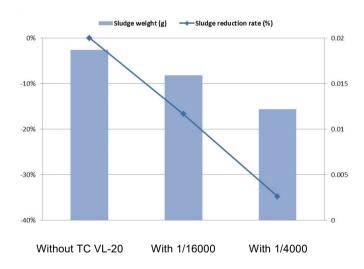
TAICRUSH VL-20 is a fuel additive that suppresses sludge precipitation caused by poor storage and mixing stability of solvent compatibility, which is a concern when using a fuel oil that meets SOx emission regulations from 2020 VLSFO (Very Low Sulfur Fuel Oil) residual oil grade (RM... Residual Marine Fuel).

With the new formulation, the sludge suppression power is about twice as much as before, that means the dosing amount is about half (compared to our conventional product), and the sludge generated due to the characteristics of VLSFO is strongly suppressed.

Dispersing sludge in the fuel oil in a fine state contributes to the cleanup of FO tanks, strainers, purifiers, piping, etc.

Check the stability of the fuel oil using a test kit and prevent the sludge trouble by adding the optimal amount of fuel oil according to the fuel oil.

This product also has a sludge suppression effect against HSFO used on ships equipped with SOx scrubbers.



## Sludge suppression effect for single oil of VLSFO



TAICRUSH VL-20 (dosage 1/16000) Without With TC VL-20

## [How to use]

The standard dosage rate of TAICRUSH VL-20 is 1/16000.

If there is a concern about fuel mixing stability / single stability using a test kit (Compatibility and Stability Test Kit), adjust the dosage rate against fuel oil. (up to 1/2500)

It also has a sludge suppression effect on HSFO used on ships equipped with SOx scrubbers.



Sludge suppressant and dispersant for 2020 SOx regulatory FO



[How to use the test kit / judgment method]

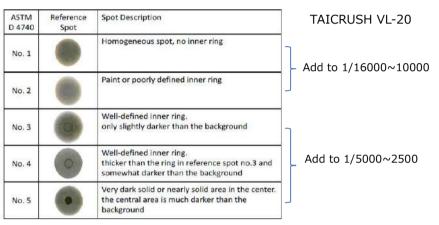
Sampling of the bunkering fuel, the FO from the ship's FO tank, and with the mixed fuel oil, a spot test will be conducted using a test kit.

After testing, adjust the dosage rate of TAICRUSH VL-20 according to Reference Spot No. before use.

\* Please use the test kit referring to the instruction manual.

Compatibility and Stability Test Kit

Dosage rate of TAICRUSH VL-20 (reference example)



The above dosage rates are based on in-house tests by Ichinen Chemicals. The contents may be updated depending on the properties of the compatible oil to be produced in the future

## [Dosage method]

Dose appropriated amount of TAICRUSH VL-20 directly into the storage tank before bunkering. In the fuel tank TAICRUSH VL-20 mixes uniformly with fuel oil by convection.

Add an appropriate amount to the settling tank when switching FO (fuel oil mixing).

[General properties]

Classification	Oiliness
Appearance	Light yellow transparent liquid
Specific gravity	0.92 (at 20°C)
Viscosity	50 mPa•s (at 20°C)
Flash point	65°C

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ICHINEN CHEMICALS CO.,LTD.

This document, and more, is available for download from Martin's Marine Engineering Page - www.dieselduck.net

## Attachment 4

## Documents provided by ADEKA CORPORATION

Problems with Fuel Switching to Low Sulfur Fuel Oils and Approach (Sludge Dispersant: ADEKA ECOROYAL SD-20)

Problems of Low Sulfur Fuel Oils and Approach (Fuel Additives: ADEKA ECOROYAL Series)

## Problems with Fuel Switching to Low Sulfur Fuel Oils and Approach (Sludge Dispersant : ADEKA ECOROYAL SD-20)

## ADEKA CORPORATION

## 1. Introduction

As global cap on sulfur content in bunker fuel starts, HSFO will become unusable on vessels without scrubbers since January 1, 2020. Therefore, fuel switching is needed within 2019. It is important to make the sulfur content of the fuel oil 0.5% or less safely and economically, and how to restrict the sludge generation is a key. In this article, the precautions for tank cleaning and fuel switching, and the features with application examples of our sludge dispersant "ADEKA ECOROYAL SD-20" are described.

## 2. Forms of sludge in the FO storage tank

## 2.1 Before tank cleaning

There are various images about the sludge forms in the tank and can be roughly classified into the following three patterns. Although the condition of each vessel differs depending on the properties of the bunker fuels used up to now and the history of the use of additives, dry sludge does not often exist as a mass at the bottom of the tank, it's considered that there remains unpumpable residual oil and some viscous sludge.

- 1) Dry sludge that has accumulated and solidified for a long period of time at the bottom of the tank
- 2) Viscous sludge with particulate sludge suspended in the fuel oil
- 3) Only unpumpable HSFO residue, sludge-free

## 2.2 After tank cleaning

In the step of bunkering the low sulfur fuel oil (VLSFO or LSMGO), there is a risk that new sludge is generated due to fuel blend with HSFO residual oil. Table 1 shows sludge generation when HSFO and LSMGO are mixed, and it is understood that sludge generation becomes remarkable in a certain fuel mixing range. Similarly, in VLSFO where the blended type will be the main stream, light fraction such as LSMGO is used as a cutter stocks, and sludge generation is also concerned when HSFO and VLSFO are mixed because of the differences in kinematic viscosity and density. Furthermore, the use of a sludge dispersant is considered to be important because sludge generation due to fuel compatibility is concerned when VLSFO are mixed with each other.

Sludge	HSFO/LSMGO mixing ratio (w/w)					
dispersant	1/0	1/2	1/4	1/8	1/20	1/99
None			0	0	0	0

**m-11.1** Club 

ADEKA Corporation Functional Chemicals Development Laboratory R&D Division Keiichi Odagiri / Manager (k-odagiri@adeka.co.jp), Taro Sumi

## 3. Dispersion and removal of sludge deposited in the FO storage tank

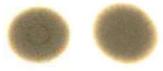
It is preferable to clean tanks before bunkering the low sulfur fuel oil (VLSFO or LSMGO), but this is not preferable from an economic point of view because it may be off-hire in some case. In order to remove the sludge at the bottom of the tank without stopping the vessel, the tank is cleaned by adding sludge dispersant into HSFO repeatedly. Approach according to the form of the sludge is described as follows.

## 3.1 Dry sludge

It is difficult for additives to diffuse and permeate into bulky dry sludge, and removal using sludge dispersant or other chemicals is not easy. Since it is unlikely that the insoluble dry sludge rapidly peels off and dissolves into the low sulfur fuel oil, it is expected that there is no high possibility that the sulfur content rises. It is considered that even if the dry sludge is peeled off, it can be removed by the purifier, but as a precautionary approach, adjustment of the bunkering speed is also effective. Physical tank cleaning is necessary, and it is considered that there is no problem if the tank is cleaned at the dock next time.

## 3.2 Viscous sludge

Particulate sludge prior to dry sludge can be dispersed and stabilized in HSFO by adding sludge dispersant. In our experiments, it was confirmed that the condition of sludge dispersion was improved by adding SD-20 to HSFO (Figure 1). In addition, even if SD-20 is added to the fuel oil in which sludge is precipitated by fuel blend in advance at the fuel mixing ratio at which sludge is apt to occur, improvement of the condition of sludge dispersion has been observed (Figure 2).



w/o additive 1/10

1/10000 added

Figure 1. Effect of SD-20 to HSFO



w/o additive



tive 1/200 added Before fuel blend



1/200 added After fuel blend

**Figure 2.** Influence of timing of SD-20 addition to mixed fuel (HSFO/LSMGO=1/8, w/w)

## 4. Prevention of sludge generation due to fuel blend at fuel switching and approach

The most important thing in fuel switching is to reduce the sulfur content of the fuel oil to 0.5% or less safely without sludge generation. If a large amount of HSFO residual oil remains, sludge may occur at the time of fuel switching. Therefore, it is desirable to minimize the amount of HSFO residual oil by adjusting trim, heel, temperature, and so on before bunkering the low sulfur fuel oil.

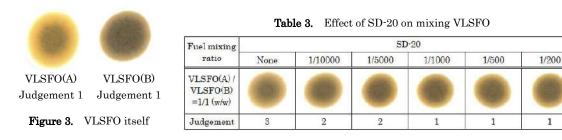
Addition of sludge dispersant is effective to actively restrict sludge generation during fuel blend. There is a minimum amount necessary for sludge dispersant to form the reverse micelle structure and disperse and stabilize the sludge, and the dispersion ability and the necessary amount of sludge dispersant differs depending on its chemical structure, fuel mixing ratio, and so on.

It can be seen in the Table 2 that SD-20 shows good sludge dispersion ability by adding 1/500 to 1/200 at the mixing ratio of the fuel oils in which sludge is apt to be generated. At the time of fuel switching, it is important to determine the amount of sludge dispersant by considering the mixing ratio of fuel oils without sticking to the normal amount of sludge dispersant added to HSFO.

Fuel mixing	SD-20					
ratio	None	1/5000	1/1000	1/500	1/200	
HSFO/LSMGO =1/4 (w/w)	0	0	0	0	0	
HSFO/LSMGO =1/8 (w/w)	0	0	0	0	0	

Table 2.	Effect of SD-20 at some fuel mixing ra	itio
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When switching to VLSFO, there are problems of its stability and fuel compatibility. Addition of sludge dispersant is considered to be effective when sludge occurs over time due to inferior its stability. On the other hand, even if VLSFO itself is "judgement 1" as in the case of Figure 3, if VLSFO are mixed in a ratio of 1:1, "judgement 3" is obtained because of inferior fuel compatibility. It was confirmed that SD-20 showed good sludge dispersion ability even in VLSFO, since it was improved up to "judgement 1" according to the dosage of SD-20.



On the other hand, sludge generation by mixing aromatic type and paraffinic type of VLSFO has been suggested, but it is difficult to judge the type from the certificate of analysis. Until the properties of VLSFO settle down, it is important to purchase fuel oils from bunker traders who provide physical supplies and to increase the amount of sludge dispersant.

#### 5. Approach to switch piping system from HFSO to low sulfur fuel oil

Fuel system is as follows: FO storage tank  $\Rightarrow$  Settling tank  $\Rightarrow$  Purifier  $\Rightarrow$  Service tank  $\Rightarrow$  Viscosity controller  $\Rightarrow$  Auto back wash filter  $\Rightarrow$  Main engine or generator. The points of the subsequent steps after FO storage tank are described below.

#### 5.1 Settling tank, service tank

Since the settling tank and the service tank are controlled so that the fuel levels are constant, fuel blend is inevitably avoided and sludge may occur. Normally, since the temperature is set to about 90degC, the kinematic viscosity is lower than that of the FO storage tank, which is a factor that makes sludge more likely to occur.

Even if sludge dispersant has already been introduced into the FO storage tank, it is considered useful to pay attention to the operating conditions of the purifier and to additionally introduce sludge dispersant into settling tank, and so on.

When VLSFO process is started, it is preferable to reduce the throughput of the purifier, to perform parallel operation or to shorten the blowing interval, and to carry out open inspection at an early timing to confirm the state of sludge separation. Some VLSFO have a density close to that of LSMGO, but it is considered that purification is required.

In the service tank, coarse sludge may accumulate due to operation failure of the purifier, and sludge may flow from the fuel outlet valve at the bottom of the tank, resulting in a trouble of the equipment. ECL SHIPMANAGEMENT CO., LTD (ECLSM), a ship management company of EASTERN CAR LINER, LTD (ECL), which has been cooperating in developing fuel additives, has installed floating high suction in the service tank for three years. By supplying the fuel oil from the supernatant portion with less sludge to the engine, the occurrence of trouble in the main engine is reduced. Increased the amount of sludge collected during tank cleaning at the dock were observed, and the number of backwashes of auto back wash filter was reduced.

## 5.2 Auto back wash filter

The number of backwashes of the filter may increase. It is considered that coarse sludge larger than filter mesh size of  $10 \sim 30 \mu m$  is generated by fuel blend. Therefore, addition of sludge dispersant for restricting aggregation of asphaltene sludge is effective.

## 6. Our sludge dispersant (ADEKA ECOROYAL SD-20)

## 6.1 Mechanism

"ADEKA ECOROYAL SD-20" is a sludge dispersant developed by focusing on fuel blend at the time of fuel switching or the use of VLSFO. From the Stokes equation (1) representing the sedimentation rate (V) of the particle, sludge generation factors associated with fuel blend include a decrease in kinematic viscosity ( $\eta$ ), an increase in density difference between sludge and fuel oil ( $\rho_0$ - $\rho$ ), and an increase in particle size due to sludge aggregation (a).

$$\boldsymbol{V} = \frac{2a^2 \left(\rho_0 - \rho\right)g}{9\eta} \tag{1}$$

Since the kinematic viscosity and the density difference depend on the property of the fuel oil, it is considered effective to prevent the increase of the particle diameter (a) in order to restrict sludge generation. SD-20 wraps asphaltene sludge like a surfactant, disperses and stabilizes sludge in the fuel oil, and restrict sludge generation derived from aggregation.



Figure 4. Image of sludge dispersion by SD-20

## 6.2 Evaluation by filter test

Asphaltene sludge is a black solid insoluble in the fuel oil and can be collected by a filter. The fuel oil in which SD-20 was added to HSFO/LSMGO=0.5/99.5 (w/w) was passed through the filter, and the amount of sludge generation was compared from the weight gain of the filter. When the sludge dispersant was not used, the amount of sludge generation was compared. It was confirmed that the amount of sludge generation was reduced according to the dosage of

SD-20 (Figure 5). It is also considered that the sludge is dispersed without aggregation because the appearance of the filter becomes thinner from black.

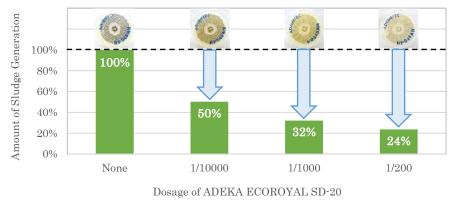


Figure 5. The result of filter test

#### Evaluation by dispersion stability test 6.3

In order to check the influence on the sludge sedimentation rate, SD-20 was added to the fuel oil mixed at HSFO/LSMGO=1/8 (w/w) to measure the change in transmitted light intensity over time. It can be determined that the smaller the change in transmitted light intensity in the height direction of the sample, the more stably the sludge is dispersed and harder the sludge is sedimented. From Figure 7, it was confirmed that sludge sedimentation rate (slope) became smaller and the condition of sludge dispersion became stable according to the dosage of SD-20.

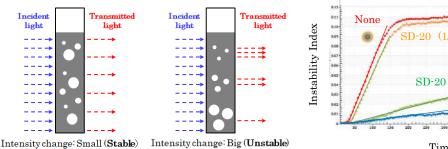


Figure 6. Transmitted light intensity and sludge dispersion

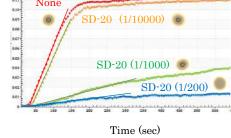


Figure 7. Dispersion stability test

#### 6.4 Confirmation of the performance by a third party

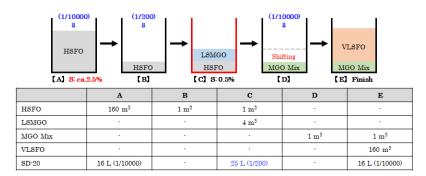
In the presence of the inspector, the performance of SD-20 was checked and the ClassNK certificate "Statement of Fact" was obtained.

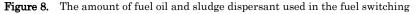
## 7. Fuel switching operation

Experiments were conducted in a manner suited to the handling of the fuel oil in the vessel, and the effectiveness of operations using SD-20 was verified. VLSFO samples supplied in major ports were obtained with the help of ECLSM. As described in 3 and 4 above, we have focused on that not only the sludge in the FO storage tank is dispersed and removed, but also the fuel oil is switched safely without generating sludge, and the sulfur content of the fuel oil is reduced to 0.5% or less. The points of the operation are shown below.

- 1) To minimize sludge generation, reduce HSFO residual oil to unpumpable state
  - · Reduce consumption of LSMGO and SD-20 by adding to minimum amount of HSFO
- 2) Use required minimum amount of LSMGO to flush FO storage tank
  - $\cdot$  Dilute the sulfur content to 0.5% or less
  - · Reduce the viscosity of HSFO residual oil to make them easier to remove
  - · Assist in the diffusion of sludge dispersant into the tank divided into multiple sections

3) Add 1/200 of SD-20 to achieve sufficient sludge dispersion at a predetermined fuel mixing ratio









[A] HSFO + SD-20 (1/10000)
 [C] HSFO/LSMGO (1/4) + SD-20 (1/200)
 [E] MGO mix + SD-20 (1/10000)
 Figure 9. Sludge dispersion status at each step

Since LSMGO has low flash point and is difficult to heat, fuel oil and SD-20 were mixed and evaluated at room temperature. Significant sludge reduction was observed at every stage, and it was confirmed that SD-20 had higher sludge dispersion ability (Figure 9). The fuel switching operation described above is considered to be capable of completing the fuel switching safely, promptly and cost-effectively without sludge generation. At present, fuel switching is in progress in the vessels managed by ECLSM.

[Contact] ADEKA Corporation, Functional Materials Department, Group-3 Phone: +81-3-4455-2834 Inquiry form (https://www.adeka.co.jp/en/chemical/inquiry/inquiry.html)

## Problems of Low Sulfur Fuel Oils and Approach (Fuel Additives : ADEKA ECOROYAL Series)

## ADEKA CORPORATION

## 1. Introduction

VLSFO and LSMGO can be considered as low sulfur fuel oils to comply with the global cap on sulfur content in bunker fuel from 2020. In this article, the problem of fuel oils and fuel additives for oils are described.

## 2. Problems of low sulfur fuel oils

Table 1 shows the fuel concerns of VLSFO and LSMGO. It is important to use the fuel additives in consideration of the types and properties of the fuel oil to be used and the operating area.

## 3. Fuel compatibility (Sludge Dispersant : ADEKA ECOROYAL SD-20)

There is a concern of sludge generation at the time of fuel switching. Since the stability of VLSFO itself may not be sufficient, therefore, the use of sludge dispersant is recommended until the quality of VLSFO is stable. Please refer to the article entitled "Problem and Approach for Fuel Switching to Low Sulfur Fuel Oils" for our sludge dispersant "ADEKA ECOROYAL SD-20".

## 4. Cold flow property (Cold Flow Improver : ADEKA ECOROYAL CF-11)

The fuel oil (VLSFO or LSMGO) contains a wax component called n-paraffin (long alkyl chain hydrocarbons), and the wax may solidify at low temperature to reduce the fluidity of the fuel oils. When the FO storage tank or other equipment cannot be heated, the fuel supply line or the filter is blocked, making it difficult to transfer the fuel oil, and there is a concern that an engine stoppage trouble may occur. Some of the VLSFO samples obtained in main ports have low pour point around 10degC, and we have to pay attention to use this kind of the fuel oils.

The cold flow improver changes the fluidity of the fuel oil by refining the wax crystals precipitated at low temperature. We're developing "ADEKA ECOROYAL CF-11" for VLSFO and plan to commercialize it within 2019.

Keiichi Odagiri / Manager (k-odagiri@adeka.co.jp), Taro Sumi

ADEKA Corporation Functional Chemicals Development Laboratory R&D Division

## Table 1. Problems of low sulfur fuel oils

	VLSFO	LSMGO
Fuel Compatibility	0	
Cold Flow Property	0	0
Lubricity	(0)	0
Mold Generation	1	(0)



w/o additive 1/200 added

Figure 1. Effects of SD-20 (HSFO/LSMGO=1/8)





## 5. Lubricity (Anti-Wear Agent : ADEKA ECOROYAL AW-37F)

The fuel injection pump or other equipment is self-lubricated by the fuel oil, and the fuel itself need to have lubricity. As the sulfur content of the fuel oil decreases, there is a concern about the wear in sliding parts such as pumps and nozzles. The amount of wear affects not only the sulfur content but also the kinematic viscosity. However, since the kinematic viscosity at 50degC is expected to be set to 20cSt or more in VLSFO to be supplied domestically, the wear risks are considered to be smaller than expected. However, some of the VLSFO samples obtained in main ports are below 5cSt, we should be careful when bunkering overseas.

On the other hand, since the sulfur content of LSMGO is lower than 0.01% and the kinematic viscosity is low, there is a concern that the wear would increase due to the low lubricity.

Our anti-wear agent "ADEKA ECOROYAL AW-37F" adsorbs to sliding metal surfaces and restricts the wear by reducing direct metal-to-metal contacts. In the HFRR test, it was confirmed that the wear scar diameter was reduced to less than 460µm (recommended by engine manufacturers) by adding AW-37F to LSMGO.

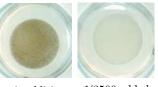


w/o additive 1/2500 added Figure 3. Effect of AW-37F

#### 6. Mold generation (Anti-Fungal Agent : ADEKA ECOROYAL AF-50)

In case of scrubber failure, low sulfur fuel oils (LSMGO) is loaded on the scrubber ship. Since HSFO is heated and used with high kinematic viscosity, mold is hardly generated, but since LSMGO has low kinematic viscosity and does not need to be heated, mold is easily generated. When stored in the FO storage tank for a period of time, the strainer or other equipment is blocked due to mold generation, making it difficult to transfer the fuel oil, and there is a concern that an engine stoppage trouble may occur.

Our anti-fungal agent "ADEKA ECOROYAL AF-50" is added to fuel oils to suppress mold growth. In the antifungal test in which the condition in the fuel tank was assumed, it was confirmed that the fungus growth was suppressed by adding AF-50 to LSMGO.



w/o additive 1/2500 added Figure 4. Effect of AF-50

[Contact] ADEKA Corporation, Functional Materials Department, Group-3 Phone: +81-3-4455-2834 Inquiry form (https://www.adeka.co.jp/en/chemical/inquiry/inquiry.html)

## ClassNK

Booklet for ship crew members Precautions concerning change-over to 0.50% sulphur compliant fuel oils [First Edition]



Booklet for ship crew members Precautions concerning change-over to 0.50% sulphur compliant fuel oils [First Edition] [English]

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