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CIMAC Guideline

Marine fuel handling in connection to stability and compatibility

By CIMAC WG7 Fuels

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1 Scope

This guidance aims to provide a practical and working understanding of the definition of stability and compatibility of marine fuel oils and how these two specific fuel properties may be best managed in the supply chain and on-board ships.

This complements and expands on the information given in ISO/PAS 23263:2019 “Considerations for fuel suppliers and users regarding marine fuel quality in view of the implementation of maximum 0.50% Sulphur in 2020” (hereafter referred to as “the PAS”). The PAS has been written to support the International marine fuel standard ISO 8217:2017, to which this guideline will also refer.

Details on the accepted available test methodologies for stability and for predicting compatibility are included, covering their applicability and correct interpretation. All stakeholders involved, in the supply and/or use of marine fuel oil are invited to adopt this guidance as ‘the common industry approach’ on the subject matter.

2 Introduction

Essentially all existing marine fuels, distillates and residuals, are to some degree mixtures or blends of a range of hydrocarbon fractions both in terms of the base hydrocarbon products from which they have been produced and from subsequent blending, to meet certain specification requirements.

Already a factor of existing fuels, marine fuel stability is addressed in ISO 8217:2017 by test method ISO 10307-2. It is the responsibility of the supplier to ensure that the fuel as delivered is stable.

It is the responsibility of the engineers on board to apply best practice fuel management to mitigate the risk of mixing incompatible fuels; this is best achieved through defining a ship specific storage segregation strategy and where this cannot be avoided by applying a concise commingling plan. Various methods are available for determining the compatible nature of a specific fuel with other fuels.

This document provides an overview of the commonly accepted and available test methods applicable to fuel stability. In addition, the methods that can be used to evaluate compatibility between fuels, either by direct testing and/or through forward prediction will be covered.

2.1 Stability in the context of IMO 2020

Traditionally, for the residual fuels, blending was principally in terms of viscosity control but then, with the greater availability of high-density refinery products, density also became a blending factor. The increasing restrictions on marine fuel sulphur content, defined by MARPOL Annex VI Regulation 14.1.3, have changed the primary blend target from viscosity and density to sulphur.

Whereas viscosity and/or density are at a relatively consistent level within the same fuel grades in the pre-2020 fuels, the implications of this mean that marine fuels post 2020 are expected to result in a wide variability of fuel formulations and characteristics alike.

Despite this variability in characteristics against a single ordering specification, CIMAC still recommends all marine fuels be purchased under ISO 8217:2017¹ in its entirety². In addition, the fuels shall be sulphur compliant in accordance to statutory requirements.

3 PART 1 – Understanding Stability and Compatibility

3.1 The complexity of residual fuel oils

It is important to appreciate that residual marine fuel's chemical composition is difficult to define as it much depends upon the source of the crude oil and the manufacturing processes. The constituents of a residual fuel however include asphaltenes, resins and liquid hydrocarbons.

The generic term 'asphaltene' covers a wide range of heavier hydrocarbon structures of high molecular weight and high carbon/hydrogen ratios, the exact constituents being dependent on the crude source and choice of blend stocks. The nature of the liquid hydrocarbons will determine the fuel's capability to maintain the asphaltene in suspension and remain in a stable condition allowing this important source of energy to take part in the combustion process. (See Annex A for a more detailed chemical explanation).

If the asphaltene cannot be retained in their suspended (colloidal) state, they will drop out as sludge and the fuel has become unstable. Any break in the suspension results in an irreversible unstable condition, with potential serious operational implications, the likes of which are explained later in this document.

The terminology used when talking about the risk of asphaltene precipitation is:

- **Stability:** The fuel as supplied
- **Compatibility:** The ability of two fuels forming a stable mix when commingled
- **Stability Reserve:** A measure of the ability of an oil to maintain asphaltene in a dispersed state and prevent flocculation of the asphaltene

3.2 Stability

Since asphaltene-free fuels cannot precipitate asphaltene sludge by themselves, it is not applicable to discuss asphaltene stability for such fuels.

The stability of a residual fuel is defined by its resistance to precipitate asphaltene sludge despite being subjected to forces, such as thermal and ageing stresses, while handled and stored under normal operating conditions.

ISO 8217:2017 specifies that fuels must be stable.

¹ This guideline can also be used in conjunction with earlier editions of ISO 8217 when an earlier edition is included in the commercial agreement between seller and buyer

² See also ISO/PAS 23263:2019

3.2.1 Factors influencing stability

Fuel formulation

The first influence is in the formulation of the fuel blend itself. It is the responsibility of the supplier to formulate the blend to ensure that the fuel is stable and that the fuel's stability reserve is sufficient (see 3.4) to withstand the anticipated influences and conditions on board ship.

Thermal and mechanical stresses

The main influences on board ship are the direct thermal and mechanical stresses likely to be faced during storage, handling and through centrifugal treatment.

Storage time

Extended storage time can degrade the fuel to eventually break up, become unstable and deposit asphaltenic sludge.

Since there is no definitive way of assessing how long a fuel will remain homogenous and stable during storage, handling or treatment on board, it is recommended to apply "first-in first-out" principle on the use of fuel batches (see CIMAC Recommendation 25). Prior CIMAC advice has suggested to use fuels within 6 months, however, with the introduction of VLSFOs this period might need to be reduced.

3.3 Compatibility

Compatibility is the term used for the ability of two or more fuels to be comingled without evidence of material separation; or in other words, no asphaltenes precipitating when the fuels are mixed. It should be noted that two perfectly stable fuels can be incompatible resulting in asphaltenic sludge precipitation when mixed. In addition, two fuels may be compatible at some mixing ratios and incompatible at other mixing ratios – or they can be compatible or incompatible over the entire mixing ratio.

3.4 Stability Reserve

Stability reserve is an indication of the capacity for one fuel to absorb another fuel without asphaltenes dropping out of suspension. Several factors, e.g. the nature of the actual asphaltenes and the nature of the fuel oil, impact this capacity.

Part 2 of this CIMAC guideline describes test methods that might be used to obtain information on the stability reserve.

Currently ISO 8217:2017 does not include test methods that indicate stability reserve.

3.5 Consequences of unstable fuel

Fuels which are unstable are essentially unusable since the precipitated asphaltenes, together with the entrained fuel, forms excessive sludge concentration in tanks and can readily choke purifiers, filters, fuel injection equipment and even fuel lines themselves. Under such conditions fuel treatment is often impossible and even transfer becomes problematic. In the case of thermal instability, problems will normally be encountered in the purifier or service system fuel oil heaters.

In either case, even if great care and focus are taken in using the onboard cleaning system, the precipitated material can form a hard adhering, coke like material which is not easily removed other than by manual means.



Figure 1: Examples of asphaltene sludge precipitation

The consequence therefore of a ship having an unstable fuel in its system can be severe and the only resolution is very often to manually remove the fuel from the tanks, unblocking pipe work, heaters, filters and other fuel system components, if necessary.

From a ship perspective, the impact of an unstable fuel is identical to the impact of having mixed two incompatible fuels, however, the responsibilities are very different. It is the responsibility of the supplier to provide a stable product whereas it is the responsibility of the engineers on board to apply best fuel management practice to mitigate the risk associated with mixing incompatible fuels.

3.6 Practical steps mitigating the risk of a fuel becoming unstable on board

It requires knowledge of fuel characteristics and their compatible nature to effectively apply precautionary measures handling and using marine fuels in order to mitigate potential risks and associated consequences.

The ship's primary objective when managing fuels on board should be to avoid mixing two differently sourced fuels and segregating the different fuels during storage. It is recognized however, that some degree of commingling on board the ship may be difficult to avoid, particularly in the fuel transfer, settling, service and supply circuits e.g. when switching between fuels and having to load on top of the 'unpumpable' fuels remaining in the storage tanks below the suction level.

Thermal stresses can lead to the fuel in storage becoming unstable. Consequently every efforts should be taken to prevent the fuel being unnecessarily heated over extended periods.

The following steps may be considered for mitigating the risks of either receiving an unstable fuel or creating an incompatible mixture through inadvertently commingling on board.

Stability as supplied:

1. Order the fuel to the ISO 8217:2017 specification which includes the stability test method ISO 10307-2
2. Select supplier considering recommendations in the guidance document MEPC.1/CIRC.875 'Best practices for purchasers.'
3. Request the Certificate of Quality (CoQ) from the supplier prior to receiving bunker and compare characteristics with that of fuels already on board. Widely diverse characteristics to one another, such as density, viscosity and carbon residue may indicate potential incompatibility issues
4. Be proactive in minimising mixing of fuels especially fuels with widely different properties
5. Perform compatibility tests between all fuels, even if segregation is applied, either on board and/or in laboratories on shore
6. If mixing in tanks is anticipated, ensure compatibility checks are made between the two fuels in accordance with the anticipated ratio and in the order of mix prior to commingling (see Chapter 4). For each compatibility test run, ratios of around 10/90, 50/50 and 90/10 are recommended as a minimum. If the mixing ratio is known, compatibility testing should be done using the actual ratio between existing fuel in the tank and the new fuel to be loaded on top.
7. Maintain a record of the compatibility between fuel tanks
8. Apply "first-in first-out" fuel inventory principle

4 PART 2 – Test methods explained

4.1 Introduction

The industry offers a number of options for confirming the stability of the fuel and to test for the compatibility between fuels. Whilst stability requires just the one fuel to undergo the test, the compatibility test to date has always required a sample of both fuels to be available in the laboratory or on board the ship for the test to be carried out.

A comprehensive review of the test methods on the market has shown that there are test methods available which – without having both fuels in the same laboratory - can provide some level of prediction of the compatibility between two or more fuels.

In this section, all the main test methods on offer today will be addressed and their suitability, advantages and disadvantages for use on marine residual fuels will be identified.

4.2 Test methods for evaluating stability and compatibility

There are a number of listed test methods for evaluation of stability and compatibility, however, not all are sufficiently reliable for use on residual marine fuels.

By testing the stability of a mixture of two or more fuels, it is possible to obtain an indication of the compatibility between the mixed fuels.

Table 1 lists the test methods suitable for determining the stability of marine residual fuels.

Test method	Reference	Applicability		
		Stability	Compatibility (=stability of mixture)	Prediction of compatibility without testing
Total sediment (TSE, TSP, TSA)	ISO 10307 (ASTM D4870, IP 375/390)	✓	✓	No
Spot test*	ASTM D4740	✓	✓	No
S-value	ASTM D7157	✓	✓	✓
P-value	ASTM D7112	✓	✓	✓
P-ratio	ASTM D7060	✓	✓	✓

* Accuracy will be impacted by waxy fuels (see section 4.4)

Table 1: Test methods which are available and can be applied to marine fuels

Table 2 lists other test methods which are not further discussed in this guideline for one or more of the following reasons:

- do not have criteria for evaluating the stability or compatibility of fuels; and/or
- are not standardized; and/or
- require significant scientific recognition and cross industry experience to uniformly apply and interpret

Test method	Reference
Separability Number	ASTM D7061
Toluene Equivalent (TE)	N/A
Xylene Equivalent (XE)	N/A
Bureau of Mines Correlation Index (BMCI)	N/A
BMCI / CCAI / TE / XE	N/A

Table 2: Test methods which cannot be applied to predict compatibility

4.3 Sediment methods

Common for the sediment test methods is that they can be used to evaluate the stability of a fuel or compatibility when testing the sediments of a mixture between fuels.

Compatibility between two fuels cannot be predicted through the individual sediment results of the fuels.

4.3.1 ISO 10307-1 (Existent Total Sediment, TSE)

TSE measures the amount of sediment present in a fuel at a particular moment by filtration and weighing the amount of sediment on the filter. TSE includes organic and inorganic sediment.

4.3.2 ISO 10307-2 (Potential Total Sediment, TSP - Procedure A)

TSP is the total sediment after ageing a sample of residual fuel for 24h at 100°C under prescribed conditions i.e. the amount of sediment after stressing the fuel through heating.

This method is expected to show the maximum amount of sediment that is likely to form when applying thermal stress.

4.3.3 ISO 10307-2 (Accelerated Total Sediment, TSA - Procedure B)

TSA is the total sediment after dilution of a sample of residual fuel with a paraffinic solvent (hexadecane) under carefully controlled conditions, followed by storage for 1h at 100°C i.e. the amount of sediment after stressing the fuel chemically and storage at 100°C for 1 hr.

This method is expected to show the maximum amount of sediment that is likely to form when applying a combination of chemical and thermal stress.

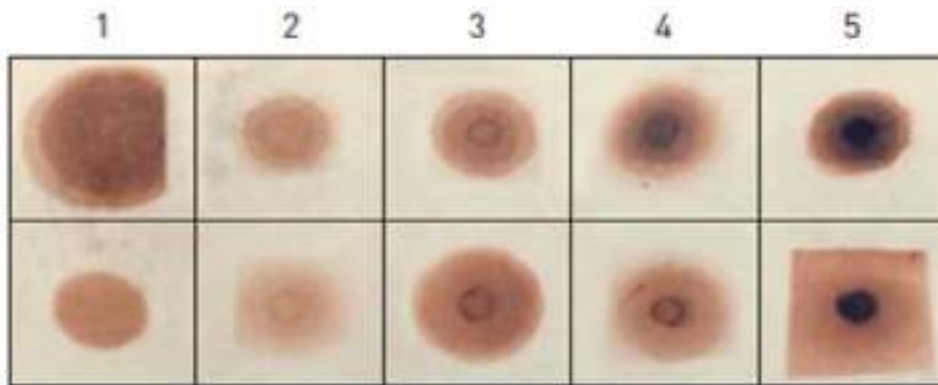
4.4 ASTM D4740 (Cleanliness / compatibility)

This test requires that one of the fuels is a residual fuel oil as, otherwise, there will be no asphaltenes to drop out. The method is designed for two purposes:

1. The determination of the cleanliness of residual fuel oil (fuels containing asphaltenes); and
2. The compatibility of a residual fuel oil with a blend stock applicable for fuel oils with viscosity up to 50 cSt at 100 °C.

A drop of a fuel (1) or a blend of two or more fuels (2) is put on a test paper and heated to 100°C. After 1h, the test paper is removed from the oven, the resultant spot is examined for evidence of precipitation and rated for stability against ASTM D4740 '5 level rating' scale. When a spot is more

distinctive in the centre of the filter paper, it indicates that asphaltenes have dropped out which implies that the fuel or mixture of fuels at the blending ratio is unstable.



Spot rating description:

- 1 : Homogeneous spot (no inner ring)
- 2 : Faint or poorly defined inner ring
- 3 : Well-defined thin inner ring, only slightly darker than the background
- 4 : Well-defined inner ring, thicker than the ring in reference spot No. 3 and somewhat darker than the background
- 5 : Very dark solid or nearly solid area in the center. The central area is much darker than the background

Spot rating interpretation (See Annex B for further images of the spot test):

- Ratings 1 and 2 indicate the two fuels are compatible in the used mixing ratio
- Rating 3, Caution
- Rating 4 and 5 indicate the fuels are incompatible in the used mixing ratio

4.4.1 Limitation of the spot test method

Whereas the spot test method (ASTM D4740) is the practical option for onboard evaluation of the compatibility between fuels, it has certain limitations that it is important to take note of:

- Waxy (more paraffinic) fuels may result in a false negative interpretation, i.e. indicate that the fuels are incompatible although they are actually compatible
- Care should be taken evaluating spots that are not clearly distinctive (as the examples in Figure 2). In case of doubt, it is recommended to segregate fuels and await analysis results from the laboratory

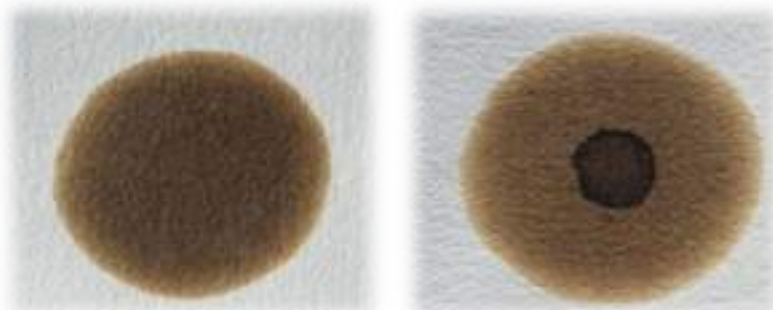


Figure 2: Two very distinctive spots being a rating of 1 and 5 respectively

4.5 ASTM D7157, ASTM D7112 and ASTM D7060

These methods generally all involve:

- addition of an aromatic solvent (e.g. toluene/xylene/methylnaphthalene)
- titration with a non-aromatic solvent (e.g. heptane,hexadecane)
- optical detection of asphaltenes precipitation for determining stability parameters or parameters that can be used for guidance on compatibility of crude oils or fuels

A summary of the methods is provided in Table 3.

	ASTM D7157 (Rofa)	ASTM D7112 (Porla)	ASTM D7060 (Zematra)
Stability parameters	Sa, So and S-value *	SBN, IN, Po, Pa, P-value *	FR _{max} and Po *
Scope	HFO, residues, crude oils Asphaltenes > 0.5%	HFO, residues, crude oils Asphaltenes > 0.05%	HFO, residues, Asphaltenes > 1.00%
Principle	Determination of intrinsic stability of asphaltenes in an oil	Determination of stability & compatibility by titration and optical detection of precipitated asphaltenes	Determination of the maximum flocculation ratio and peptizing power
Sample quantity	1 to 9g	20g	5 to 9g
Duration of analysis	60 to 90 minutes	60 to 90 minutes	40 to 180 minutes

*Refer to 4.5.1 for the definition of the terms

Table 3: Comparison of the test methods for the determination of stability parameters

4.5.1 Terms

Stability

Parameters related to the stability of a fuel are:

- S- and P-value, P-ratio (see 4.5.4): intrinsic stability
 - Indication of the stability or available solvency power of an oil with respect to precipitation of asphaltenes
 - The higher the value, the better the stability
- So and Po: peptizing power of the oil medium
 - Ability to dissolve an asphaltene or maintain an asphaltene in colloidal dispersion
 - The higher the value, the better the capability of the fuel oil matrix to keep the asphaltenes dispersed
- Sa and Pa, FR_{max}: peptizability of asphaltenes
 - Ability of asphaltenes to remain in a colloidal dispersion
 - The higher the value, the higher the capacity of the asphaltenes to remain dispersed

The relationship/balance between So, Po and Sa, Pa and FR_{max} provides information on the level of stability reserve of a fuel oil although stability reserve is not a quantified parameter.

Compatibility

Blending model parameters which can be used to obtain guidance on compatibility of fuels:

- SBN : Solubility blending number
 - Measure of the oil's ability to keep asphaltenes in solution
- IN : Insolubility number
 - Measure of the degree of asphaltenes insolubility
 - A higher number indicates a higher risk for asphaltenes precipitation

Only parameters obtained from the same test method can be used to obtain indication on the degree of compatibility e.g. results of ASTM D7157 (Rofa) cannot be used in combination with results of ASTM D7060 (Zematra) or ASTM D7112 (Porla).

4.5.2 ASTM D7157

Analysis according to ASTM D7157 provides the Sa, So and S-value from which the SBN and IN can be derived [1]:

$$IN = 100 \times (1 - Sa)$$

$$SBN = IN \times (1 + (S-1) \times \text{density} / 1000); \text{ where density must be in kg/m}^3$$

A fuel is considered unstable when the S-value is below 1. The higher the S-value, the less risk of asphaltenes precipitating from the fuel.

4.5.3 ASTM D7112

Analysis according to ASTM D7112 provides the Solubility Blending Number (SBN) and the Insolubility Number (IN) in addition to Po, Pa and P-value.

A fuel is considered unstable when the P-value is below 1. The higher the P-value, the less risk of asphaltenes precipitating from the fuel.

4.5.4 ASTM D7060

Analysing according to ASTM D7060 provides the FR_{max} and Po. Po/FR_{max} is called the P-ratio and a fuel is considered stable when the Po is higher than the FR_{max} , i.e. when P-ratio = Po/FR_{max} is greater than 1. The higher the P-ratio, the less risk of asphaltenes precipitating from the fuel.

4.5.5 Compatibility model: ASTM D7157 and ASTM D7112

The oil compatibility model is based on Solubility Blending Number (SBN) and Insolubility Number (IN) and the following approximations:

- The maximum IN, IN_{max} , of the two fuels (i.e. the less stable asphaltenes) is the limiting factor
- SBN varies linearly

The model takes the mixing ratio of the two fuels into consideration by calculating the volumetric average of the SBN's of the individual fuels, SBN_{mix} :

$$SBN_{mix} = \% \text{ Fuel}_A \times SBN_{, \text{fuel A}} + \% \text{ Fuel}_B \times SBN_{, \text{Fuel B}}$$

Recognising the complexity of asphaltene stability, a certain degree of uncertainty is considered by means of introducing a “margin for error”. In the criteria below a factor of 1.4 [2] is used:

Stable mix: $SBN_{mix} > 1.4 * IN_{max}$
Critical mix: $IN_{max} < SBN_{mix} < 1,4 * IN_{max}$
Unstable mix: $SBN_{mix} < IN_{max}$

Table 4: Compatibility model applicable for ASTM D7157 and ASTM D7112

Example 1 :

Fuel	SBN	IN
Fuel A	90	41
Fuel B	69	17
<i>Blend of fuel A and fuel B; Ratio 50/50</i>	$SBN_{mix} =$ $(0.50 \times 90) + (0.50 \times 69) = 79.5$	$IN_{max} = 41$ $1.4 \times IN_{max} = 57.4$

The Fuel A and Fuel B mix meets the stability requirement of Table 4 (as $SBN_{mix} > IN_{max}$) and is therefore considered to be stable. The interpretation can also be illustrated as shown in Figure 3.

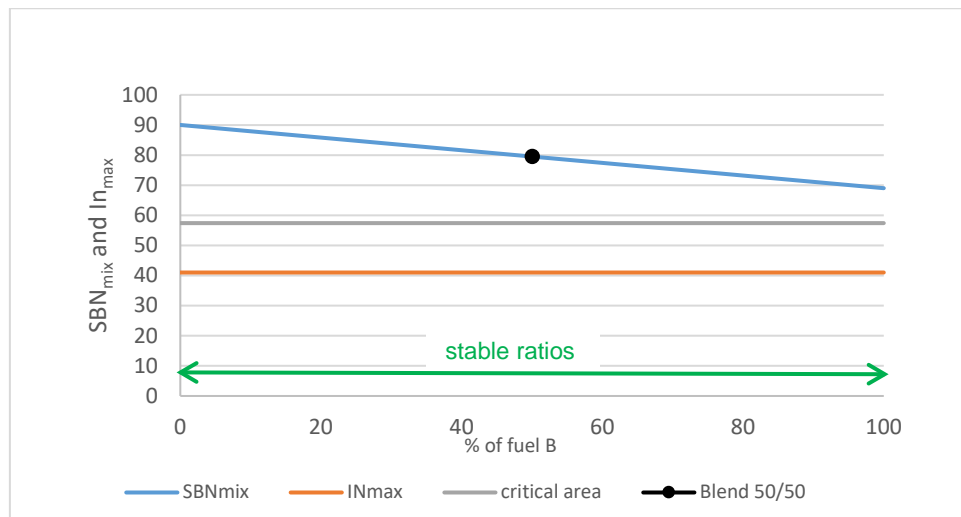


Figure 3: Interpretation of compatibility between Fuel A and Fuel B

Example 2:

Fuel	SBN	IN
Fuel C	79	39
Fuel D	13	24
<i>Blend of Fuel C and Fuel D; Ratio 10/90</i>	$SBN_{mix} =$ $(0,10 \times 79) + (0,90 \times 13) = 19,6$	$IN_{max} = 39$ $1.4 \times IN_{max} = 54.6$

The 10/90 mix between Fuel C and Fuel D does not meet the requirement of Table 4 (as $SBN_{mix} < IN_{max}$) and is therefore considered unstable. The interpretation is illustrated in Figure 4.

From the graphical presentation, it can be seen that mixing the two fuels in a 50/50 ratio is predicted to be a critical mix and that mixing in 90/10 ratio is predicted to be a stable mix.

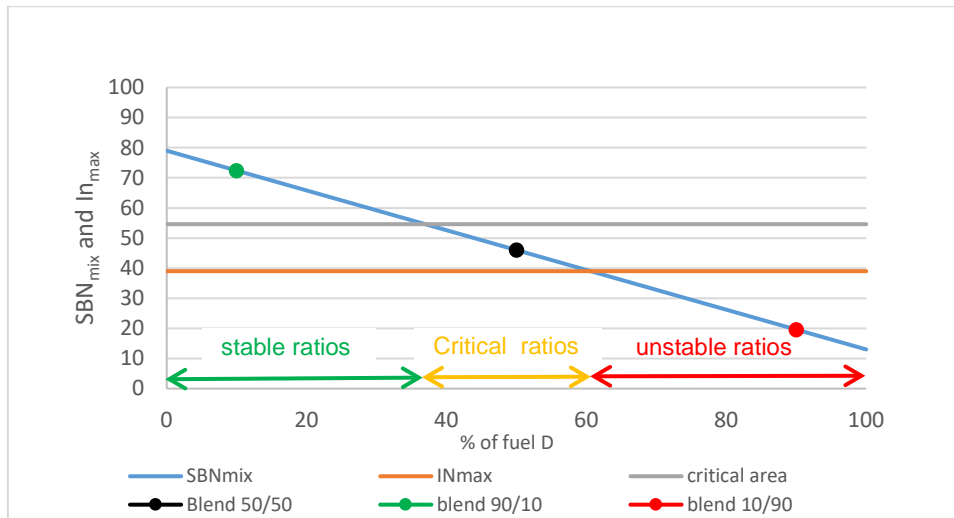


Figure 4: Interpretation of compatibility between Fuel C and Fuel D

4.5.6 Compatibility model: ASTM D7060

For ASTM D7060, the following compatibility model applies:

- $FR_{\max(\max)}$: The highest of the FR_{\max} 's of the two fuels
- $Po_{(\text{mix})}$: The volumetric average of the Po 's of the individual fuels

Whereas the ASTM D7157 and ASTM D7112 applies a margin for error to take uncertainties into account, the data from ASTM D7060 better compare with the ones from the other two methods if no margin for error is applied. This might be because of the different solvent and titration agents imply more stringent parameters.

Example 3:

Fuel	FR_{\max}	Po
Fuel E	27	51
Fuel F	63	110
Blend of Fuel E and Fuel F; ratio 90/10	$FR_{\max(\max)} = 63$	$Po_{(\text{mix})} =$ $(0,90 \times 51 + 0,10 \times 110) = 56,9$

Figure 5 illustrates the unstable area where $Po_{(\text{mix})} < FR_{\max(\max)}$. Mixing in the ratio of 90/10 between fuel E and F is predicted to result in an unstable mix. The fuels are incompatible when mixed in ratios below 20.3% of fuel F.

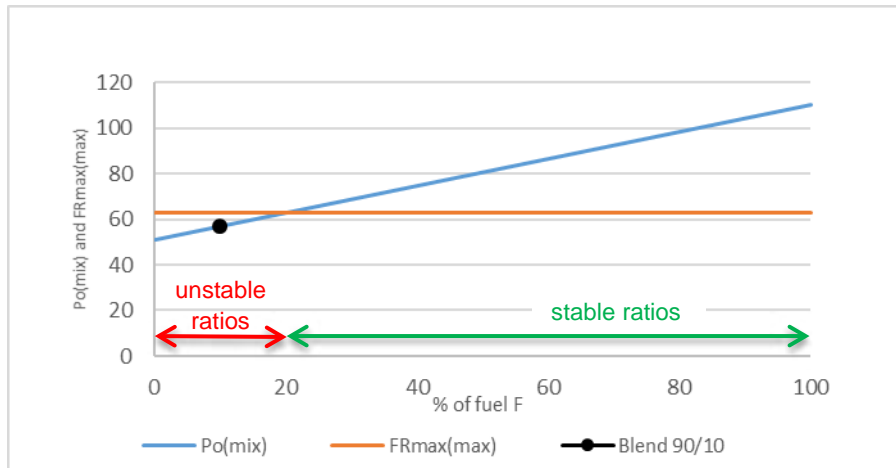


Figure 5: Compatibility diagram for fuels E and F based on ASTM D7060

Example 4:

Fuel	FR_{max}	Po
Fuel G	50	93
Fuel H	86	107
Blend of Fuel G and Fuel H	FR _{max(max)} = 86	

Figure 6 illustrates that Fuel G and Fuel H are predicted to be compatible over the entire mixing ratio.

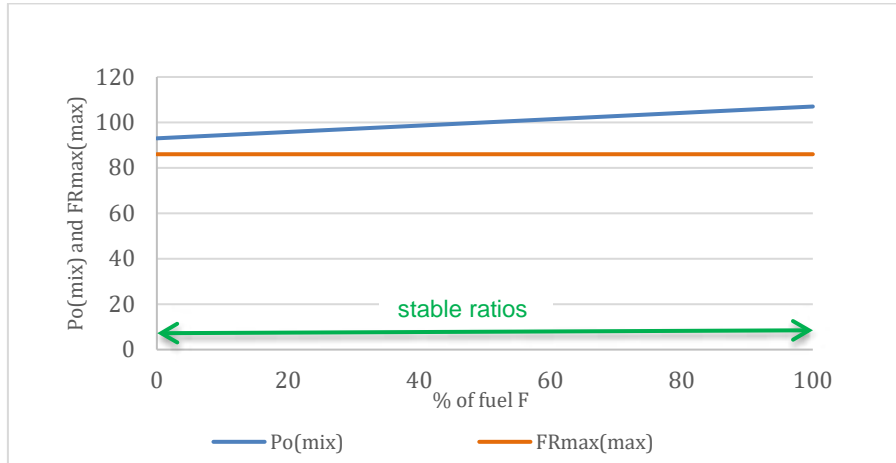


Figure 6: Compatibility diagram for fuels G and H based on ASTM D7060

5 Summary / Conclusions

Stability and compatibility of marine fuels both relates to asphaltenes dropping out of suspension resulting in asphaltenic sludge being formed.

Stability is the term used for fuels as supplied and as per ISO 8217, it is the responsibility of the fuel supplier to provide a stable fuel to the ships.

Compatibility is the term used when evaluating if two (or more fuels) can be mixed without asphaltenes coming out of suspension. As such compatibility is a handling issue and the responsibility of the operator.

From an operational perspective, the result of having an unstable fuel or having mixed two incompatible fuels, causing the fuel mixture to become unstable, is identical as asphaltenic sludge will precipitate in the storage tanks, block filters and or separators leading to operational problems. Good practices therefore need to be applied to minimise the risk of having to manage an unstable fuel on board.

Several test methods to evaluate fuel stability exist have been highlighted in this paper, however, their applicability and accuracy varies. Not all have been standardised and some neither have sufficient scientific recognition nor industry experience to apply for marine fuel oils, at present.

Only one method (ASTM D4740) is available as providing a useful onboard screening tool for compatibility between two fuels of which one must be of a residual (RM) nature. It should be noted that this method can give a higher rating number when waxier fuels are involved potentially resulting in a false negative result, i.e. fuels which are actually compatible may be deemed less compatible or incompatible by the method.

The most effective way to determine a fuel's stability or compatibility between two or more fuels, is using test methods that can only be applied in a controlled laboratory setting.

The test method ISO 10307-2 Potential Total Sediment (TSP) is used as the definition for a stable fuel in ISO 8217:2017 when the TSP is below 0.10% m/m.

The three test methods: ASTM D7157, D7112 and D7060 with the prediction model offer a tool to evaluate the degree of compatibility of fuels without the need to test the fuels mixed together. Before applying the predictive models, the fuels shall be tested by the same test method for comparative purposes. Whilst these three test methods may be used for determining stability of a fuel and to predict the degree of compatibility, they are less practical as a routine test method where the TSP (ISO 10307-2) remains applicable and can be more easily run along with ASTM D4740.

6 Members of CIMAC WG7 Fuels

Alfa Laval

Boll Filter

BP Oil International Ltd

Bureau Veritas fuel testing services

Caterpillar

CEPSA

Chevron

Chevron Oronite

CMA Ships

DNV-GL

Exxon Mobil

French Ministry of Defense

GEA

IMarEST

Infineum

Innospec Fuel Specialties

International Chamber of Shipping

Intertek Shipcare

Lloyd's Register FOBAS

Maersk Line

MAN Energy Solutions

Japan Engine Corporation

Mitsui O.S.K. Lines

NYK Line / Nippon Yuka Kogyo

Parker Hannifin

Petroleum Geo-Services

Shell

Total

VISWA Lab Corporation

VPS

Wartsila

Win GD

World Fuel Services

7 References

[1] US58771634A - Process for blending potentially incompatible petroleum oils, I Wiehe, R Kennedy, 1999

[2] Concawe report 11/19, Study to evaluate test methods to assess the stability and compatibility of marine fuels in view of the IMO MARPOL Annex VI Regulation 14.1.3 for 2020 Sulphur requirements

8 Glossary of important, repeating terms

PAS	Publically Available Specification
ULS MGO	Low sulphur Marine Gas Oil, Sulphur max 0.10% (m/m) (no heating required)
HS MGO	High sulphur Marine Gas Oil, Sulphur above 0.10% (m/m) (no heating required)
ULSFO RM	Ultra low sulphur fuel oil, Residual properties, Sulphur max 0.10% (m/m) (heating required)
ULSFO DM	Ultra low sulphur fuel oil, Distillate properties, Sulphur max 0.10% (m/m) (no heating required)
VLSFO RM	Very low sulphur fuel oil, Residual properties, Sulphur max 0.50% (m/m) (heating required)
VLSFO DM	Very low sulphur fuel oil, Distillate properties, Sulphur max 0.50% (m/m) (no heating required)
LSFO	Low sulphur fuel oil, Sulphur max 1.00% (m/m), (heating required)
HSFO	High sulphur fuel oil, Sulphur above 1.00% (m/m), (heating required)

9 Annex A

9.1 What can influence stability - the chemistry explanation

In order to have a deeper understanding of asphaltene stability it can be helpful to grasp the basic chemistry of Residual Hydrocarbon Products (RHPs), the base components for fuel oil blending, not least it demonstrates the complexity of the residual marine fuel that ships so readily use. RHPs are streams recovered as residual products from different conversion units, after separation of the lighter products (distillates) has been carried out via distillation. The chemical matrix of RHPs is much more complex than the one in the distillates, but a high-level classification can be carried out on the basis of the separation achieved via SARA analysis (Saturates, Aromatics, Resins and Asphaltenes).

Saturates

Saturates are the sum of paraffins and naphthenes, i.e. organic molecules that do not contain double bonds. Naphthenes differ from paraffins because they are cyclic structures.

Paraffinic chains can be bound to naphthenic rings in more complex structures.

Aromatics

Aromatics are components containing one or more benzene rings. Paraffinic chains can be bound to aromatic rings in more complex structures.

Asphaltenes

Asphaltenes are a complex array of different molecular structures with very high molecular weight. The backbone is made of aromatic rings fused together and/or bound to each other via paraffinic chains. They also contain a certain amount of 'heteroatoms' (nitrogen, oxygen, sulfur) and heavy metals (such as Nickel and/or Vanadium), which are bound to the backbone through the heteroatoms.

Asphaltenes are also defined as the fraction of RHPs which is soluble in toluene but not in a specific paraffinic solvent. If that solvent is n-heptane, those asphaltenes are defined as "C7-asphaltenes". If that solvent is pentane, those asphaltenes are defined as "C5-asphaltenes".

Asphaltenes are not really 'dissolved' in the RHP matrix, but they are rather 'peptized', i.e. they tend to form very finely dispersed agglomerates, which under certain circumstances, can coalesce and precipitate as sludge. This is a typical behaviour of colloidal dispersions.

Resins

Resins have a similar structure to asphaltenes but their molecular weight is lower and they have a negligible metals content. Resins are usually defined at an operational level as the fraction of RHPs that is soluble in n-heptane and pentane but insoluble in liquid propane. This definition is, however, not universal and the way resins are identified in different refinery layouts can vary considerably. It can be said that they represent an "intermediate" between asphaltenes and saturates/aromatics.

Maltenes

The sum of saturates, aromatic and resins constitutes the maltenes.

9.2 Asphaltene stability

The stability of asphaltenes depends on a delicate balance with the maltenes, mostly based on the basic chemistry concept that 'like dissolves like'. As asphaltenes have a substantial aromatic character, they tend to be stabilized by predominantly aromatic maltenes (such as light cracked streams).

The presence of resins also brings a stabilization factor, as they tend to form a 'bridge' between asphaltenic agglomerates and the rest of the maltene phase.

Saturates, on the other hand, tend to have a detrimental effect on asphaltenes stability, as their chemistry is very different. Their interaction with asphaltenes is generally lower than for aromatics and resins. Among the saturates, the waxy streams (such as hydrocracker bottoms and high pour point vacuum gasoil), show the worst effect on asphaltenes stability due to their high paraffinic character.

Among different types of asphaltenes, a higher polarity will also negatively influence the solubility behaviour in a maltene phase. Polarity is related to the amount of heteroatoms in the asphaltene structure and it can increase for some types of asphaltenes due to oxidation processes, if such asphaltenes are exposed for a long time to air.

An additional factor influencing asphaltene precipitation is temperature, especially in the presence of crystallized paraffinic waxes at low temperature. If waxes separate from the maltene phase at lower temperature as crystals, that phase will increase its solubility power for asphaltenes, which may give a high apparent solvency power for the asphaltenes in that sample. As the temperature increases, more waxes get dissolved back into the maltene phase, decreasing its solvency power and potentially result in asphaltene flocculation.

The following illustration demonstrates the process by which a stable fuel will become unstable and precipitate asphaltenes, when mixed with another incompatible fuel.

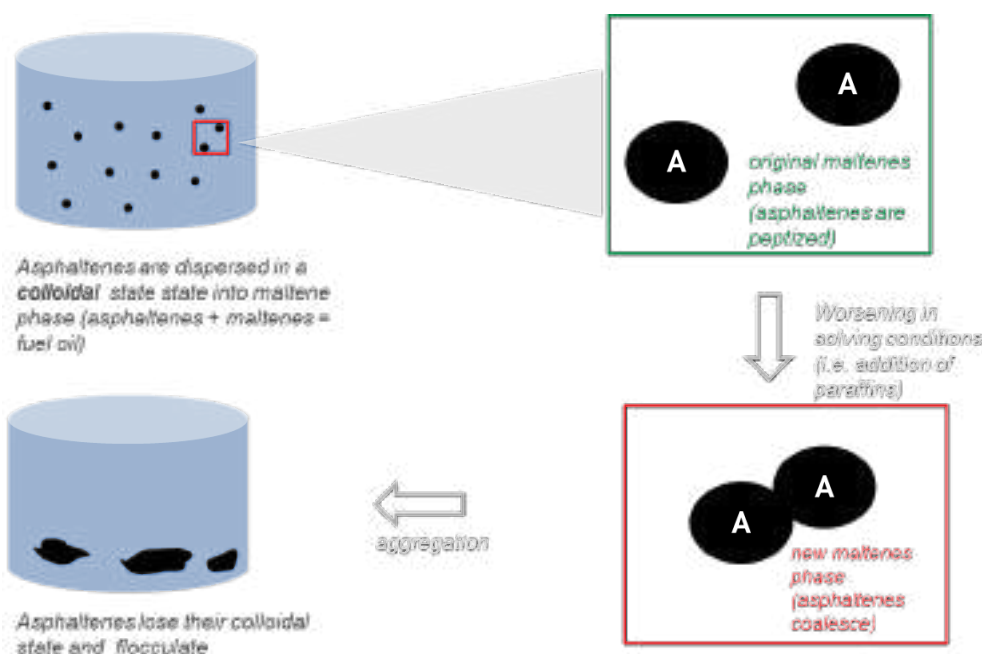
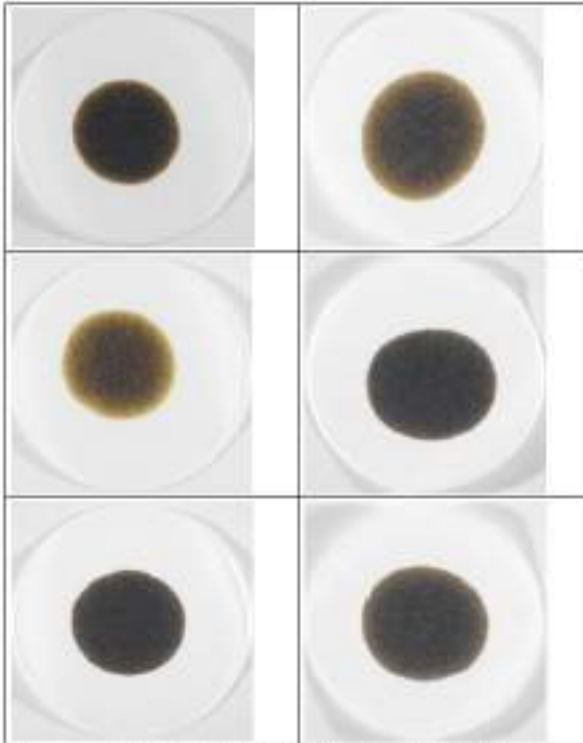
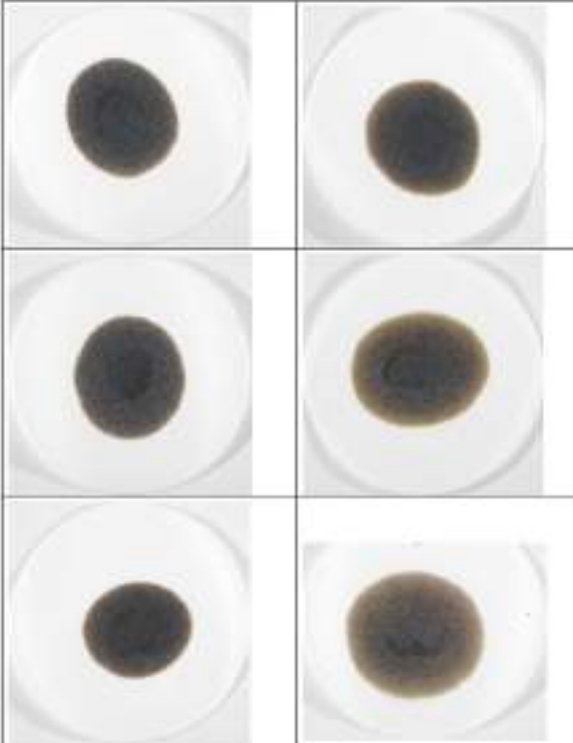


Figure 7: Asphaltene stability in maltenes

10 Annex B – ASTM D4740 – Reference ‘Spot test’ images

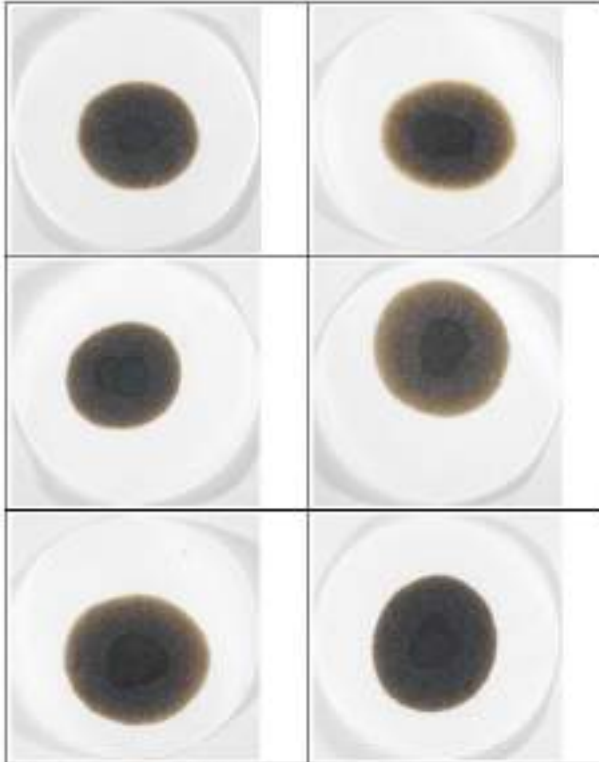
The following tables illustrate further examples of the ‘spot test’ filter results (images supplied by kind permission of NYK Line / Nippon Yuka Kogyo).

Rating 1	Rating 2
<p>No inner ring, homogenous spot.</p> <p>The fuel mix is stable, two fuels mixed are compatible at tested ratio.</p>	<p>Faint or poorly defined inner circle</p> <p>The fuel mix is stable, two fuels mixed are compatible at tested ratio.</p>
	

Rating 3

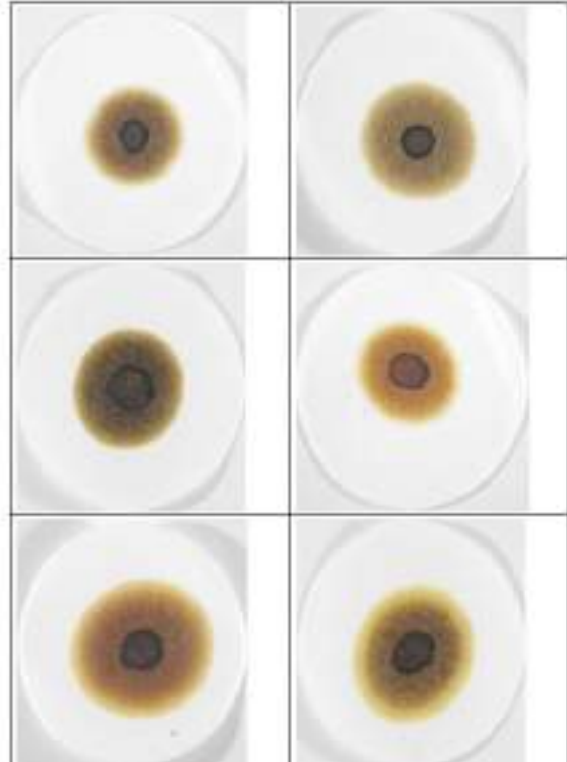
Well-defined thin inner ring, only slightly darker than the background


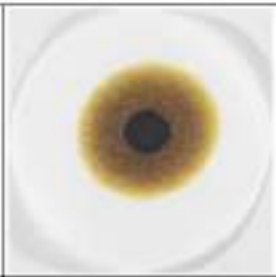

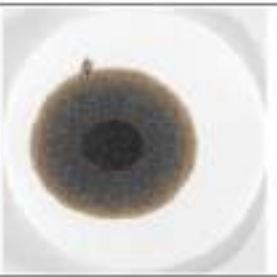








Caution: Indicates that the fuel may be incompatible in the used mixing ratio.

**Rating 4**

Well-defined inner ring, thicker than the ring in reference spot No. 3 and somewhat darker than the background

Indicates the fuels are incompatible in the used mixing ratio resulting in an unstable product.



<p>Rating 5</p> <p>Very dark solid or nearly solid area in the centre. The central area is much darker than the background.</p> <p>Indicates the fuels are incompatible in the used mixing ratio resulting in an unstable product.</p>	<p>Rating 5</p> <p>Very dark solid or nearly solid area in the centre. The central area is much darker than the background.</p> <p>Indicates the fuels are incompatible in the used mixing ratio resulting in an unstable product.</p>		
			
			
			

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