WHITE PAPER #1

COMPOUNDING.

A WINDING ROAD

SHIBATAFENDERTEAM

on the safe side

Contents.

Executive summary.

The first part of the SFT White Paper Series on fender manufacturing outlines the considerations relevant to determining what makes a good fender. It focuses on the raw materials used in rubber production, the physical properties of a fender, and their correlation with the compound's composition.

There are international standards and guidelines providing guidance as to the physical properties of rubber fenders – like PIANC2002 and ASTM D2000. However, there is no international standard specifying the chemical composition of the rubber compound used in the manufacturing of rubber fenders.

The paper finds that in fender manufacturing, physical properties are the only reliable indicator of the quality of a rubber compound that is defined by international standards. In addition, it recommends that ratios of fillers and reinforcement agents such as carbon black (CB), calcium carbonate (CC) and silica should be determined by specialists with profound material knowledge, as amount and particle size greatly influence the compound as well as its performance and durability. The paper furthermore draws attention to the fact that rubber compounds mixed correctly with CC by experienced manufacturers comply with and surpass international testing standards.

SFT White Paper Series.

Safety, reliability, durability – the performance requirements of a fender boil down to these three aspects, and rightly so. **Fenders are meant to create a safe environment for ships and passengers while protecting port infrastructures and all personnel working there – reliably during the design life and beyond.** This is the ideal that ports and port operators strive for.

In this spirit, the four-part SFT White Paper Series aims to provide an unbiased view of what exactly makes a good fender – from source materials to manufacturing process.

Part I approaches this question by taking a closer look at the constituent components of a fender and their role in determining performance-relevant physical properties. Parts II and III detail the mixing and curing processes involved in producing a high-quality rubber fender. Part IV concludes the series with a detailed report about testing.

SFT Whitepaper Series:
#1 Compounding | #2 Mixing | #3 Curing | #4 Testing

SFT White Paper Series – PART I.

As a reinforced rubber compound is the core of any fender, the first part of the SFT White Paper Series on fender manufacturing focusses on the raw materials used in rubber production, the physical properties of a fender, and their correlation with the compound's composition. Its goal is to detail the considerations relevant to determining what makes a good fender.

Yet, as straightforward as this might seem, when considering the product features required for such high performance, waters tend to become somewhat murky. There are international standards and guidelines – like PIANC2002, ASTM D2000, EAU 2004, ROM 2.0-11 (2012) or BS6349 (2014) – ensuring that fenders perform as designed when installed at a berth.

SPC Cone Fenders | IJmuiden | Netherlands

These standards provide guidance as to the physical properties of rubber fenders, among others compression set, elongation at break, and tensile strength. **There is, however, no international standard specifying the chemical composition of the rubber compound used in the manufacturing of rubber fenders.**

In other words, there are industry standards delineating a clear goal in the manufacturing of marine fenders, their performance, physical properties and durability, but there is no recommendation as to how to get there. The reason for this is simple: no two fender projects and no two fender manufacturers are alike. Each project has unique requirements that necessitate customized rubber compositions. In addition, not all polymers used in fender production are equally available in all parts of the world, requiring manufacturers to adjust their rubber compounds accordingly.

All of this provides a lot of room for market differentiation and opportunities for fender manufacturers to present their own best practice-approaches to producing high performance products. Yet, it has also become the breeding ground for some widely accepted – and by some stakeholders actively advocated – misconceptions about compound production, the most prevalent one asserting that the quality of a fender is primarily determined by the chemical composition of its rubber compound.

At the ShibataFenderTeam Group (SFT), we believe that the quality of a fender should be measured by its performance, i.e. by the degree to which a fender lives up to the requirements of its specific field of application.

The White Paper was conceived drawing on the expertise of the Deutsches Institut für Kautschuktechnologie e.V. (DIK), a German independent research institute specializing in polymeric materials and rubber technology, and of ASTM officials, as well as through previous discussions with polymer compounding specialists from the University of Gdansk, Poland.

A. Rubber compounds – the devil is in the details.

Typically, rubber fenders are made from a blend of polymers, e.g. natural rubber (NR) and synthetic rubber (SR), with fillers such as carbon black (CB), calcium carbonate (CC) and other additives to provide reinforcement and processability. **While there is a general consensus in the industry about most components used in fender production, ideas on the quality of the ingredients and their ratio diverge wildly from manufacturer to manufacturer – with some trying to establish generalizing views on the chemical composition of rubber compounds as a genuine quality indicator for the finished product.** A common misconception holds that the amount of the respective components in the rubber compound determines its quality. In the following, we will therefore take a closer look at the components constituting a rubber compound and their correlations.

Raw rubber material

Natural rubber (NR) is sourced in the form of latex from the Pará rubber tree (Hevea brasiliensis) in an area approximately 15° north and south of the Equator, with Southeast Asia being the main producer worldwide. About 40 % of worldwide rubber consumption is based on NR, which is traded as a commodity on stock markets. The geographical limitation of NR's availability and its shortage at the beginning of the 1900s led to the development of synthetic rubber (SR) in other parts of the world. Well-known and frequently used are styrene-butadiene rubber (SBR), ethylene propylene diene monomer rubber (EPDM), or neoprene. Of all the SRs, SBR is the one most frequently used for fender compounds.

SBR is a copolymer of styrene and butadiene which can be polymerized in any ratio. It is derived from petroleum byproducts and dependent on the price of cruide oil and NR. About 60 % of worldwide rubber consumption is based on SRs.

NR- and SBR-only compounds differ in their characteristics as well as their impact on compound processability, fender performance and its physical properties.

Natural Rubber (100 % NR compounds)

- + well-reinforced by nature
- + large stretch ratio (elongation)
- + high resilience
- + extremely waterproof

- – poor aging properties
- – poor oil resistance
- – susceptible to reversion (therefore sensitive to vulcanization)
- – sensitive to ozone cracking
- – as a natural product and due to the natural sourcing process, it contains impurities like protein, ash,* dirt (leaves, dust)

* Roberts, A. D. (1990). Natural rubber science and technology. Oxford: Oxford University Press

Synthetic rubber (100% SBR compounds)

- + good abrasion resistance
- + good aging stability

- – inherently poor tensile strength
- – poor heat aging resistance
- – more difficult to process

In comparison, while SBR in its pure state is less sticky and has a higher density and glass transition temperature than NR, it also has a lower modulus and tear resistance, and needs additional reinforcement and a higher amount of softeners. NR, by contrast, is well-reinforced from the outset.

Thus, rubber compounds with either NR or SBR as the only polymer have strong limitations, and therefore the industry usually uses blends of NR and SBR to harness the advantageous properties of both. If specifications require 100 % NR or SBR compounds, specifiers should make sure they are familiar with the problematic nature of these materials, since a wrong approach here could put a berth in jeopardy and could lead to substantial liability claims for the specifier.

The choice for – and the amount of – NR or SBR in the blend determines the amount of other components to be added to improve the properties of the compound, the best-known ones being carbon black (CB) and calcium carbonate (CC). The ratio in which polymers are mixed with these components defines the chemical composition of the rubber compound. Detailing the proportional relation between all components in the compound has limited informative value regarding the quality of a fender. **Two rubber compounds can differ in their chemical compositions but still have physical properties that meet or exceed the requirements of international standards (see also Table 2).** Nonetheless, it has become a commonplace for some stakeholders to argue that the presence and amount of the respective components in the compound serve as a quality indicator. A closer look at the two fillers CB and CC shows that such generalizing statements are misleading.

B. Carbon Black – essential in measures.

Carbon black (CB) is a well-established reinforcement for rubber compounds available in different particle sizes. Its capabilities are dependent not only on its amount in the rubber compound but also on its grade and particle size. Its effect can best be measured by examining the development of e.g. tensile strength when gradually increasing the amount of CB. Figure 1 illustrates how the tensile strength of the compound increases upon adding CB up to a breaking point. After reaching that critical stage, tensile strength decreases, as there is not enough rubber left to disperse the CB particles, meaning the compound is overloaded with CB.

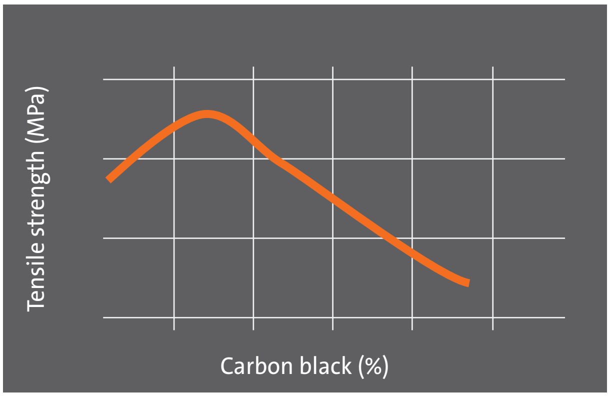

Figure 1: Typical influence of CB on tensile strength in NR compounds

This example supports the fact that the amount of CB is indeed important, but in moderation and depending on the rubber used, as NR needs less reinforcement than SBR. In other words, when it comes to the amount of CB, more is not always better. Thus, to ensure the desired compound quality, the CB concentration has to be chosen carefully at an early stage of the production process, keeping in mind all relevant factors.

On a side note, gray fenders do not contain any CB at all. As gray pneumatic, extruded and tug boat fenders make direct contact with the vessel, end-users require them to be non-marking. Since adding CB would inevitably result in a black rubber compound, they contain silica as reinforcement. And yet they comply with the same rigorous testing standards as high-durability black fenders intended for +20-year service life. **This shows again that the quality of a fender cannot be determined by the amount of CB in its rubber blend.**

Gray Pneumatic Fender | Karlskrona | Sweden

The particle size of CB is another influencing factor relevant in fender production, and much discussed in research. **It has been proven that the larger the average particle size of CB, the lower the modulus of the rubber compound, a fact supported by a great number of studies and tests.** Low modulus means that there is little force required to stretch (elongate) a specimen, which is indicative of a low-quality compound. Tests performed by Shibata Industrial in Japan prove how modulus in both NR- and SBR-only compounds with a constant dose of CB changes depending on the filler's particle size. Comparing the effects of using CB with an average particle size ranging from 22nm to 78nm, compound modulus dropped significantly the larger the particles became. Over the entire measuring range, modulus dropped by approximately 30 % with 100 % NR compounds and almost 50 % with 100 % SBR compounds (see Figure 2) – a difference incidentally proving a fact that was discussed earlier, that NR requires less additional reinforcement.

In summary, the quality of compounds cannot be gauged by their amount of CB. Compounds should therefore not be excluded from specifications only based on these grounds. The compound's component ratio and the necessary CB particle size are unavoidably bound up with a fender's desired performance and physical properties. A similar reasoning holds true for the use of CC in rubber compounds.

CB GRADES	ISAF N220	HAF N330	FEF N550	GPF N660	SRF-LM
Average particle size (nm)	22	28	45	66	78
NR 300 % modulus (MPa)	16.1	15.5	15.7	13.3	10.8
SBR 300 % modulus (MPa)	10.3	9.7	8.8	6	5.4

Table 1: Modulus vs. CB grade

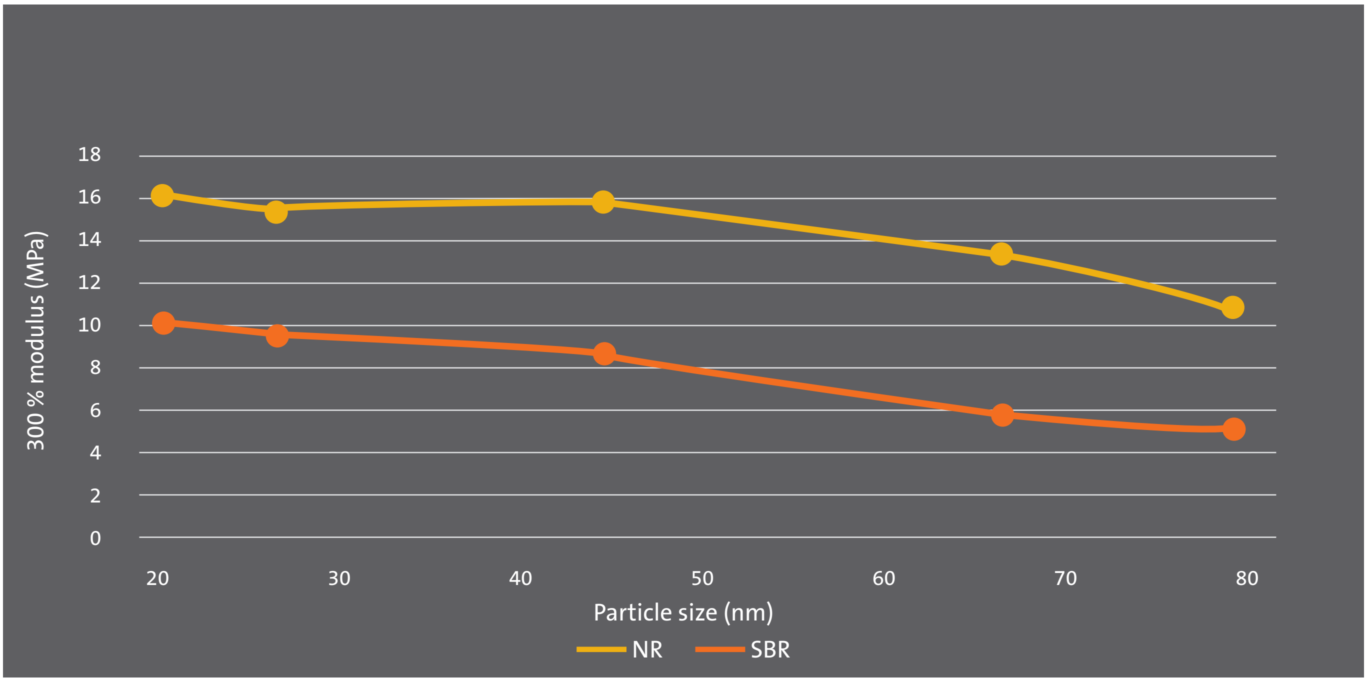

Figure 2: Modulus vs. particle size of CB (CB 33 %)

C. Calcium carbonate – better than its reputation.

Apart from CB, high-quality rubber products across the industry and beyond use several other fillers, of which calcium carbonate (CC) is the best-known. There are two different kinds of CC: natural CC and synthetic CC.

Both come in powder form, though particle sizes may vary. Adding CC enhances processability and improves behavior during vulcanization, and compression set results. Also, the right amount of synthetic CC in small particle sizes has a distinct reinforcing effect.

Despite these merits, CC has a rather bad reputation in the market. It is said to be a cheap replacement for polymers, and that it leads to poorer physical properties as well as reduced performance and durability in rubber compounds. Depending on the case, these claims might be correct; they do not, however, provide the full truth about CC.

As with CB, the origin, grade, dispersion, and above all the particle size and purity of CC determine how the filler influences the physical properties and durability of the rubber compound. Therefore, it cannot be generalized that CC only has negative effects. Used correctly, it is helpful in giving a compound physical properties that meet or even exceed international testing standards for rubber fenders.

The experts of ASTM and other institutes are unanimous in their opinion that:

> *"When it comes to rubber compounding for marine fenders, there is no standard regarding the chemical composition, as these fenders' quality is determined by their capacity to live up to the rigid performance requirements of their field of operation. As a consequence, the compound's physical properties are to be regarded as the only meaningful indicator of a rubber fender's product quality."*

CSS Cell Fenders | Yamal | Russia

D. The right compound – a winding road.

Summarizing what we have seen so far, Table 2 vividly illustrates that two rubber compounds can have very different chemical compositions and still possess the necessary physical properties to comply with required performance criteria for marine fenders, and thus meet international standards. The most important reasons for this are the different reinforcement requirements of NR and SBR. **The choice of the rubber base of the compound is dependent on the polymer's availability and the product features required in the fender.** The same causal logic also applies to the choice and amount of the other components that the rubber compound is mixed with.

As plausible as this might sound, it has become a recurring phenomenon in the fender industry to distract from this simple truth while disseminating misleading information. In this respect, wrongly asserting that the chemical composition of a rubber component is a fender's foremost quality criterion puts a dangerous spin on the facts. **Chemical composition is important in fender production, but not everything. As shown earlier, it is the physical properties that ultimately determine the quality of a fender.**

Such distortion of facts becomes problematic when subjective criteria are invoked by stakeholders as a quality indicator for fenders. A rather benign example of this concerns the density of rubber compounds. High density is considered a symptom for low quality – which is a problematic assertion when accepted without question.

CHEMICAL COMPOSITION – TGA TEST

	COMPOUND 1	COMPOUND 2
Polymer [%]	47.5	46.9
Carbon Black [%]	37.5	27.5
Residues (Ash) [%]	2.9	17.9

PHYSICAL PROPERTIES – PHYSICAL PROPERTIES TEST

PROPERTIES	TEST METHOD	SPECIFICATION	RESULT COMPOUND 1	REMARK	RESULT COMPOUND 2	REMARK
Tensile Strength [MPa]	ASTM D412 Die C – original value before ageing	≥ 16	20.20	✔	19.11	✔
Elongation at Break [%]	ASTM D412 Die C – original value before ageing	≥ 400	514.00	✔	586.08	✔
Tear Resistance [kN/m]	ASTM D624 Die B	≥ 70	127.34	✔	104.42	✔
Compression Set [%]	ASTM D395 Method B – at 70°C for 22 hours	≤ 30	19.31	✔	17.93	✔

Table 2: Compound comparison regarding chemical composition and physical properties | Compound 1 and 2 taken from fenders that have been successfully operational for years

As components like fillers and vulcanization agents have a higher density than rubber, any compound needing reinforcement is likely to have a higher density. And, as we saw earlier on, such compounds also comply with international standards. **So density is only a meaningful parameter when considered in context.**

A most striking example of this type of deception is the practice of assessing the quality of a rubber compound by subjecting it to thermogravimetric analysis (TGA).

TGA is a method of thermal analysis in which a sample – in this case of a rubber fender – is continuously weighed during heating. As different components burn off at different temperatures, the loss in weight provides an indication of the sample's composition. Certain parts, however, do not burn, even at very high temperatures and despite the addition of atmospheric oxygen. Others are released as CO_2 during the process. The non-burning parts remaining at the end are known as residues (ash).

While TGA is useful as a practical means of verifying the chemical composition of a compound, it does not provide any meaningful correlation to the quality of the compound.

Nonetheless, a high percentage of ash is erroneously considered by some as an indicator of low quality – even though there are perfectly logical reasons for residues.

As mentioned earlier, NR as a natural product contains ash, so it is not surprising that higher amounts of ash remain after burning an NR-based rubber compound. Another residue, zinc oxide, is commonly added for the curing process as a necessary vulcanization additive. Silica, which is the reinforcement agent for gray fenders (see also p. 5), does not burn either, and larger amounts of ash remain. The same applies to the aforementioned CC.

Using TGA results to discredit components that are typical in rubber production – essential even in fender manufacturing in order to meet certain requirements – must be seen not only as a misleading practice, but also as a potentially dangerous one. As mentioned before, TGA results do not allow any meaningful conclusions as to the quality of a fender or its suitability for a project. Thus, TGA results do not ensure that a fender lives up to what is expected in its field of operation. **And if a rubber fender does not perform as required, safety in marine operations cannot be ensured.**

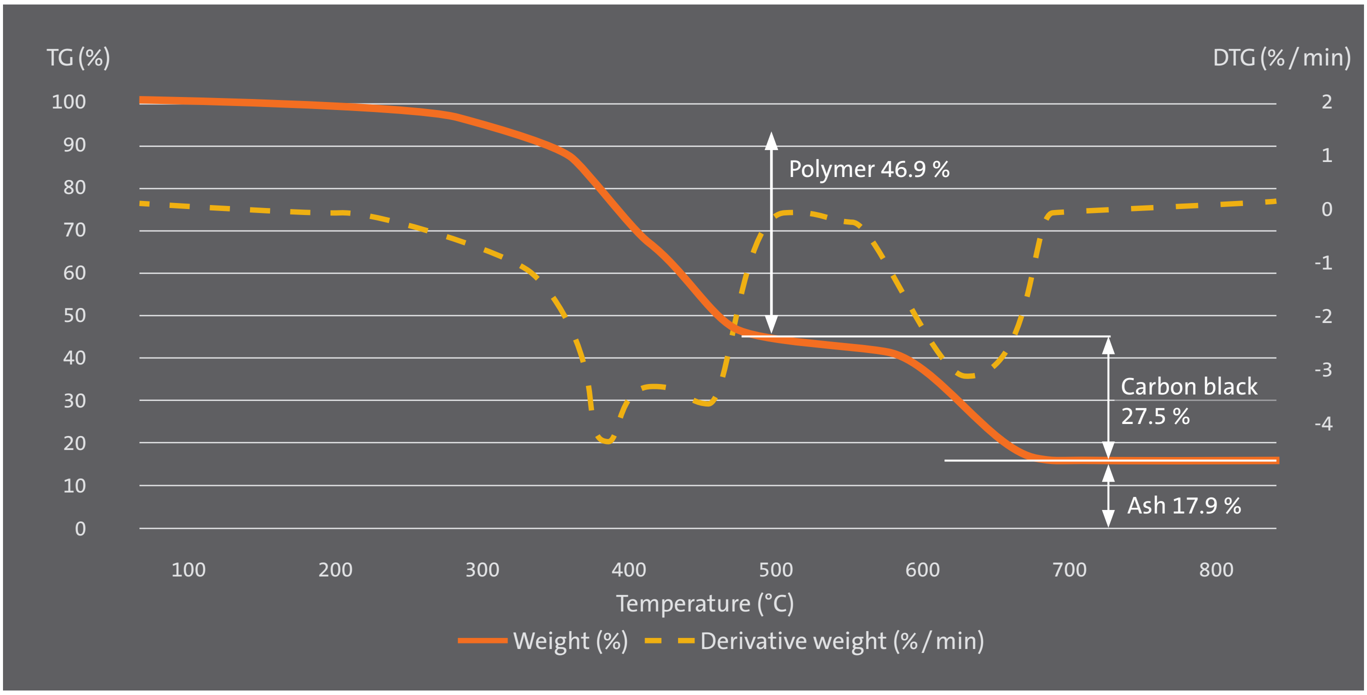

Figure 3: Thermogravimetric analysis (TGA) | Values based on Compound 2 (see Table 2)

After all, fenders are of paramount importance in securing port structures and creating a safe environment for ships and crews. Against this background, we believe that the answer to what makes a good fender not only has to reflect a high level of technical expertise, but also give evidence of a clear sense of corporate responsibility.

From the technical point of view, a good fender is the result of a combination of high-quality source materials and a fender manufacturer expertly skilled in compounding, thereby guaranteeing that the performance of the final product meets – if not exceeds – individual project requirements, and also international standards. From an ethical perspective, a good fender is the physical evidence of a corporate culture that puts the individual performance requirements of the customer first in determining product quality, and not its own need for market differentiation. In a nutshell, the quality of a fender is determined by its performance in the field, not by a fender manufacturer's claims.

As a fender manufacturer with extensive knowledge and unparalleled expertise in rubber production, we at the ShibataFenderTeam Group (SFT) believe that compounding is an expert discipline not to be taken lightly, and so project-specific that it cannot be generalized in any way. **In the end, a marine fender needs an individualized rubber compound endowing it with the right physical properties for its specific field of application.** With its white paper series, SFT wishes to advocate more transparency in fender production in order to ensure quality standards that are driven by a commitment to high-performance products and a clear sense of responsibility.

ShibataFenderTeam Group.

The ShibataFenderTeam Group is one of the leading international fender manufacturers with 50+ years of group experience in fender production, +100,000 fenders in service, and 90+ years of experience in the production of rubber products. Shibata Industrial, headquartered in Japan, is responsible for production and R&D, while ShibataFenderTeam, headquartered in Germany, handles design and sales. Their regional offices in the US, Europe, and Asia are supported by a large network of well-established local representatives on six continents.

Creating and protecting value – this is the essence of what our products are meant to do. We offer the full range of marine fender products, from simple rubber profiles to highly engineered systems, as well as accessories and fixings. Engineering excellence means that our partners can be confident in expecting the best from us in all areas. Our experience has earned us a reputation as a dependable partner in the international port, harbor, and waterways market.

info@shibata-fender.team
www.shibata-fender.team

References:

Unless indicated otherwise, all references to rubber and rubber compounding in this white paper are quoted from:
- Abts, G. (2007). Einführung in die Kautschuktechnologie *(Introduction to rubber technology)*. München: Hanser
- Hofmann, W. & Gupta, H. (2009). Handbuch der Kautschuktechnologie *(Reference guide to rubber technology)*. Ratingen: Gupta

Note:

- **Physical properties are the only reliable indicator of the quality of a rubber compound that is defined by international standards.**
- **Ratios of fillers and reinforcement agents like CB, CC and silica should be determined by specialists with a profound material knowledge, as amount and particle size greatly influence the compound, its performance and durability.**
- **Compounds mixed correctly with CC by experienced manufacturers comply with and surpass international testing standards; fenders from such compounds have a high durability and achieve a typical service life of 20+ years.**

SHIBATAFENDERTEAM GROUP.

HQ:
ShibataFenderTeam AG – Germany
+49 (0)40 63 86 10 - 170
info@shibata-fender.team

ShibataFenderTeam Inc. – USA
+1 (571) 281-3770
contact-americas@shibata-fender.team

ShibataFenderTeam S.A.S. – France
+33 (0)1 48 73 00 96
contact-france@shibata-fender.team

ShibataFenderTeam Sdn. Bhd. – Malaysia
+60 (0)3 5545 9215
contact-malaysia@shibata-fender.team

ShibataFenderTeam Spain SLU – Spain
+34 960 913 108
contact-spain@shibata-fender.team