

Aquatreat[®] AR-540

Unique Calcium Phosphate Inhibitor

Nouryon



Aquatreat AR-540 unique calcium phosphate inhibitor

AQUATREAT AR-540 is a patented, sulfonated copolymer. This polymer has evolved through a series of statistically designed experiments and commercial feedback.

Optimum inhibition of calcium phosphate in stabilized phosphate and zinc-based alkaline cooling water treatment programs is the primary objective. AQUATREAT AR-540 is a copolymer of acrylic acid and sulfonated monomers. The sulfonated monomers combine hydrophobic character, aromatic structure and high charge density. This unique combination of monomers has resulted in a copolymer with multifunctional performance characteristics. AQUATREAT AR-540 provides excellent scale and deposition control under a wide variety of conditions. Its stability under stressed conditions provides superior performance in cooling water systems operating at high cycles of concentration.

The thermal stability and unique dispersant capabilities of this polymer also prove useful in boiler applications.

The performance characteristics of AQUATREAT AR-540 have been demonstrated in laboratory bench tests, dynamic laboratory equipment and years of product sales. In all cases, the performance of this unique, new polymer has proven to be equal to or better than the old industry standard of AMPS®/Acrylate copolymers.

Features and benefits

• High-performance sulfonated copolymer: Provides effective deposit control for maximum heat transfer and optimum zinc stabilization.

- Optimum molecular weight and charge density: Effectively disperses silt. Redisperses carbonate, iron, zinc and phosphate deposits.
- Superior thermal stability: Good sludge conditioner and dispersant for boilers.

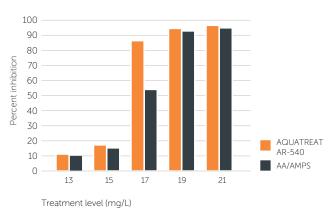
Laboratory evaluations

Calcium phosphate stabilization

AQUATREAT AR-540 is optimized to obtain maximum effect for calcium phosphate scaling under a variety of adverse conditions, including the presence of soluble iron. As the data in Figure 1 indicates, AQUATREAT AR-540 provides very effective inhibition of calcium phosphate scale and outperforms AMPS/Acrylate copolymers at lower treatment levels.

Figure 1: AQUATREAT AR-540 provides very effective inhibition of calcium phosphate scale.

Calcium phosphate inhibition



Formulation stability

Although often overlooked, a very important aspect of a polymer's utility is its stability in typical cooling water formulations. In order to demonstrate the formulation stability of AQUATREAT AR-540, cooling water formulations containing various combinations and levels of polymer, phosphate, phosphonate, zinc, molybdate and tolyltriazole were prepared. Once formulated, the stability of the solutions was observed and reported in the following tables. AQUATREAT AR-540 may not be stable in some zinc-containing formulations at pH <2.5.

Molybdate formulation

рН	13.0
Polymer at 40%	11.5%
Water	47.5%
HEDP at 60%	4.2%
NaOH at 50%	10.3%
Sodium Molybdate at 35%	24.5%
Tolyltriazole at 50%	2.0%

Result: AQUATREAT AR-540 and AA/AMPS Copolymer Stable

Stabilized phosphate formulation

рН	12.6
Polymer at 40%	11.5%
Water	57.0%
HEDP at 60%	4.2%
TKPP at 60%	18.2%
NaOH at 50%	7.2%
Tolyltriazole at 50%	2.0%

Result: AQUATREAT AR-540 and AA/AMPS Copolymer Stable

Zinc formulation

рН	13.2
Polymer at 40%	11.5%
Water	58.8%
HEDP at 60%	4.2%
NaOH at 50%	19.3%
Sodium Molybdate at 35%	2.0%
Tolyltriazole at 50%	4.2%
Pocult: A OLIATREAT AR 540 pr	d AA/AMDS Copolymor Stable

Result: AQUATREAT AR-540 and AA/AMPS Copolymer Stable

All organic formulation

pН	12.5
Polymer at 40%	23.0%
Water	50.7%
HEDP at 60%	8.3%
NaOH at 50%	14.0%
Tolyltriazole at 50%	4.0%

Result: AQUATREAT AR-540 and AA/AMPS Copolymer Stable

In order to further investigate formulation stability in a typical cooling water treatment formulation, AQUATREAT AR-540 and an AMPS/Acrylate copolymer were formulated as follows:

Ingredient	Amount ¹
Polymer	10% and 15%
HEDP	5.0%
AQUATREAT AR-900-A	10.0%
Molybdate	14.3%
Tolyltriazole	2.0%
Caustic Soda	to pH 12.5
Water	to 100%

¹ as product

Figure 2: Calcium phosphate inhibition with 10% polymer

Calcium phosphate inhibition 10% polymer

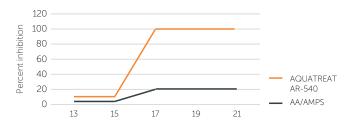
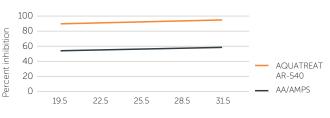


Figure 3: Calcium phosphate inhibition with 15% polymer

Calcium phosphate inhibition 15% polymer



Treatment level (mg/L active polymer)

The formulations containing AQUATREAT AR-540 and the AMPS/Acrylate copolymer were then tested for calcium phosphate inhibition using a calcium phosphate inhibition test. An unexplained loss of performance of the AMPS/Acrylate copolymer was observed in this particular formulation, while AQUATREAT AR-540 maintained the same performance it had as a neat, unformulated product. The polymers were evaluated at levels of 10% and 15% in the formulation, which accounts for the difference in treatment levels in the graphs.

Dispersing capabilities

Industrial and comfort cooling systems often contain silt, sludge and other contaminants, including corrosion products and microbial debris. The capabilities of a dispersant can be evaluated in laboratory test methods using kaolin clay. Low sludge volume and high turbidity values, as seen in Figure 4, clearly demonstrate the power of AQUATREAT AR-540.

The versatility of this product as a dispersant has been confirmed in industrial cooling tower field use, where it redisperses and stabilizes pre-existing phosphate, zinc and iron deposits. The competitive AMPS/Acrylate copolymer used as a control in this study did not produce the same beneficial results.

Figure 4: Low sludge volume and high turbidity values, clearly demonstrate the power of AQUATREAT AR-540.



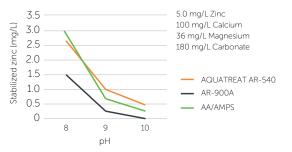
2.0% kaolin clay, 4 PPM polymer (active), 30 minutes

Zinc stabilization

Zinc is commonly used for cathodic corrosion protection in cooling water formulations. Zinc precipitates at the pH of the bulk water unless sufficiently stabilized. It is important to stabilize zinc in the system so that it is available to react at the corrosion site where the pH is higher than that of the bulk water. The selection of a polymer is critical in this application, as overstabilization of zinc will prevent it from functioning. As can be seen from the test results, both AQUATREAT AR-540 and the AMPS/ Acrylate copolymer are effective zinc stabilizers and, as expected, the homopolymer of acrylic acid, AQUATREAT AR-900A is not.

Figure 5: The graph below shows both AQUATREAT AR-540 and the AMPS/Acrylate copolymer are effective zinc stabilizers.

Zinc stabilization

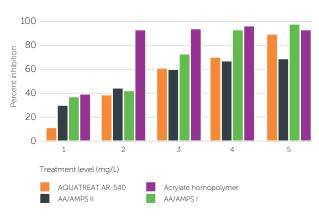


Calcium carbonate inhibition

In cooling water treatments, phosphonates and low molecular weight homopolymers are recognized as the primary calcium carbonate threshold inhibitors. The composition and molecular weight of AQUATREAT AR-540 is optimized to provide maximum protection against calcium phosphate deposition. For calcium carbonate, the major contribution of AQUATREAT AR-540 is as a dispersant and crystal modifier. However, this product does have activity as a threshold inhibitor for calcium carbonate, as demonstrated by the results obtained from the modified NACE test.

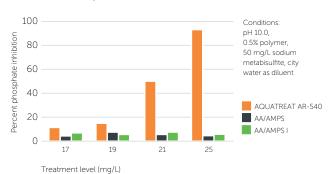
Figure 6: AQUATREAT AR-540 demonstrates calcium carbonate inhibition properties.

Modified NACE test method

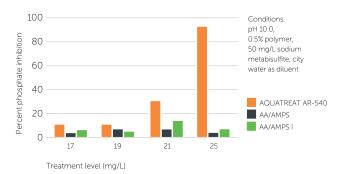


Figures 7 and 8: These graphs show AQUATREAT AR-540 being evaluated for efficacy using the Hydrothermal Stability

Four hours at 200 psi



Four hours at 400 psi



Thermal stability

Although thermal stability is not a major concern in most cooling applications, there are some instances where it may be desirable to have a polymer that does not lose its effectiveness when subjected to high temperatures. AQUATREAT AR-540 demonstrates superior thermal stability when compared to the AMPS/Acrylate polymers. AQUATREAT AR-540's thermal stability characteristics, coupled with its strong dispersing characteristics, make it a strong candidate for use in boilers. The thermal stability of these polymers was measured in a test where a solution of the polymer was exposed to pressures of 200 and 400 psi for four hours (Figures 7 and 8). Each polymer was then evaluated for efficacy using the Hydrothermal Stability test. At both 200 and 400 psi, AQUATREAT AR-540 continued to function as a calcium phosphate inhibitor, while both the AMPS/ Acrylate polymers lost their effectiveness as threshold inhibitors.

Evaluations

AQUATREAT AR-540 was evaluated in a stabilized phosphate cooling water program. The purpose of the evaluation was to determine the minimum concentration of AQUATREAT AR-540 required to stabilize 5 ppm of orthophosphate. The study was conducted over a 30-day period with variation of chemical addition and concentration as indicated in the following graphs.

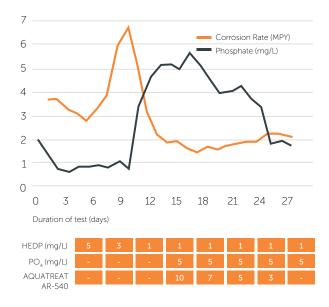
Other important operating conditions are as follows:

Calcium	160 mg/L (as Ca2+)	
Carbonate	200 mg/L (as CO32+)	
рН	8.5-8.7	
Conductivity	2,000 umhos/cm	
Flow rate	3.0 ft/sec	
Heat flux	10,000 BTU/hr/ft ²	
Bulk water temperature	90°F	

Results

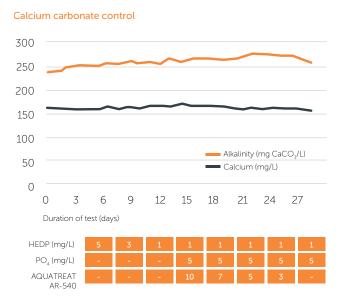
In order to determine the effect of AQUATREAT AR-540 for calcium phosphate stabilization, HEDP was added as a calcium carbonate threshold inhibitor. The minimum dosage of HEDP required was established to be 1.0 mg/L. Once established, HEDP was added at a constant rate. Next, 5 mg/L of orthophosphate was added and maintained in the system. AQUATREAT AR-540 was added at varying concentrations to determine the level required for phosphate stabilization. It was determined that a 1:1 ratio of AQUATREAT AR-540 to orthophosphate was required to demonstrate good calcium phosphate stabilization.

Figure 9: This graph demonstrates the powerful effect of AQUATREAT AR-540 as a calcium phosphate stabilizer. As stabilized phosphate increases in the system, the mild steel corrosion rate declines to an acceptable rate of 2 MPY.



Phosphate stabilization and mild steel corrosion control

Figure 10: This graph shows the ability of AQUATREAT AR-540 and HEDP to effectively prevent calcium carbonate precipitation.



Commercial use

Evaluation—first year

AQUATREAT AR-540 was compared to an AMPS/ Acrylate polymer for calcium phosphate inhibition in an industrial cooling tower. While both polymers stabilized the phosphate fed into the system, AQUATREAT AR-540 provided significant benefits. In addition to stabilizing phosphate, it redispersed and stabilized pre-existing phosphate, zinc and iron deposits. These benefits make AQUATREAT AR-540 a powerful new component for use in phosphate and zinc-based alkaline cooling water treatment programs.

The situation

An east coast pharmaceutical manufacturer used recirculating condenser water for both process and comfort cooling. Batch manufacturing processes and intermittent plant operations create a potential for scaling and deposition in the condenser water system. Strict control of mineral scaling and suspended solids deposition is required to maintain heat transfer capability. Make-up water quality and effluent regulations mandated the use of a phosphate-based corrosion control program with no acid feed. Control of calcium phosphate scaling thus became a major water treatment objective in this system. Full-scale plant tests were conducted to optimize calcium phosphate control.

The system

A two-cell 500-ton cooling tower supplies condenser water to two 250-ton York chillers. The summer basin water temperature averages about 80° F. The temperature rise across the system is about 10° F. The plant-chilled water supply temperature is 48° F with a 10° F temperature rise.

This is a relatively old system. The tower itself was in good condition, but at the beginning of the trial period, the basin contained a large quantity of a soft, brown deposit. Baseline water-quality data taken before chemical treatment is shown in Figure 11. The make-up water is good quality, with moderate hardness and conductivity and low levels of silica and suspended solids. The low pH and alkalinity indicate that this water will be very corrosive to mild steel. The circulating water analysis in Figure 11 shows that the cooling tower operates at about five cycles of concentration. The LSI value is +1.27, but the data shows no evidence of calcium carbonate precipitation. Figure 12 shows an analysis of the existing basin deposit. This material appears to be a mixture of calcium salts with corrosion products and wind-blown debris. The high loss on ignition suggests the presence of microbiological material in the deposit.

Figure 11: Water analysis before polymer feed

		Raw	Tower	
Parameter	As	Water ¹	Water ¹	Cycles
рН	рН	6.73	8.12	
Conductivity	umhos	336	1520	4.5
Total alkalinity	CaCO ₃	50.3	207	4.1
Total suspended solids	mg/L	<0.1	11.6	
Aluminum	Al	<0.1	<0.1	
Boron	BO3	0.33	2.42	
Calcium	CaCO ₃	80.3	398	5.0
Copper	Cu	0.03	0.04	
Iron	Fe	0.06	0.25	4.2
Lead	Pb	<0.01	<0.01	
Magnesium	CaCO ₃	35	175	5.0
Manganese	Mn	0.01	0.04	4.0
Molybdenum	Мо	<0.01		0.08
Sodium	Na	16	88.2	5.5
Strontium	Sr	0.16	0.77	4.8
Sulfate	SO_4	55.3	316	5.7
Zinc	Zn	0.08	0.79	
Chloride	Cl	32	177	5.5
Fluoride	F	<0.1	<0.1	
Nitrate	Ν	1.16	<0.05	
Nitrite	Ν	<0.05	<0.05	
Phosphorus-inorganic	PO_4	<0.1	2.61	
Phosphorus-organic	PO_4	<0.1	<0.1	
Phosphorus-ortho	PO_4	<0.1	<0.1	
Silica	SiO ₂	9.4	42.8	4.6
Sulfate	SO ₄	55.3	316	5.7
LSI	LSI	-1.33	1.27	

¹Chemical concentrations expressed as mg/L

Figure 12: Tower basin deposit analysis before polymer feed

Parameter	As Weight percent	
Calcium	CaCO3	42.24
Silica	SiO ₂	12.70
Iron	Fe ₂ O ₃	12.45
Zinc	Zn(OH) ₂	2.59
Magnesium	CaCO ₃	2.18
Aluminum	Al ₂ O ₃	2.08
Phosphorus	PO ₄	1.05
Sodium	Na ₂ O	0.49
Potassium	K ₂ O	0.33
All others	Percent	0.25
	Subtotal	76.37
Loss @ 850° C		32.40
	Total	108.77

The treatment program

The water treatment program, used before this field trial commenced, was based on HEDP, zinc and tolyltriazole, with no inorganic phosphate. For this evaluation, the water treatment was changed to a typical stabilized phosphate program, including 3-6 ppm molybdate as Mo, and 8-12 ppm total inorganic phosphate. HEDP was added to control calcium carbonate and tolyltriazole for copper corrosion protection. Chemicals were fed to the system by manually adjusted pumps controlled by the blowdown conductivity controller. The base water treatment program was kept constant with two different polymers evaluated for calcium phosphate control. For the first 30-day period, a commercially available AMPS/Acrylate copolymer was used. This polymer has become the industry standard for calcium phosphate stabilization. For the second 30-day period, the high-performance copolymer, AQUATREAT AR-540, was used. Each product was dosed to provide 9 ppm active polymer in the circulating water. This corresponds to a calculated inorganic phosphate to active polymer ratio of 1:1 in the product as fed to the system. Chemical treatment levels in the circulating water were maintained by a simple "bleed and feed" conductivity controller. The controller was set to maintain about 5 to 6 cycles based on conductivity.

Chemicals were fed while blowdown was on, and pump strokes were adjusted manually as required. This led to periodic over- and underfeed of chemicals, but average dosages and cycles were maintained within acceptable limits.

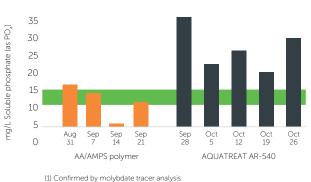
Evaluation results

Molybdate was dosed to the system at 3 to 5 ppm throughout the test. Corrosion control was satisfactory at about 2.5 mpy. Cycles based on calcium and silica held between 5 and 6 during the test period, indicating stable system operations and no precipitation of calcium carbonate.

Figure 13 shows inorganic phosphate levels in the circulating water during the two test periods. During the first 30-day period, with the AMPS/Acrylate copolymer, phosphate levels were within the expected range of 8–12 ppm based on the rate of phosphate addition to the system.

Figure 13: Solubilization of pre-existing phosphate by AQUATREAT AR-540

Total inorganic phosphate



AQUATREAT AR-540, however, showed very different behavior. Phosphate levels were well above the expected range. A reasonable explanation for these high phosphate levels is that AQUATREAT AR-540 dispersed or solubilized old phosphate deposits in the system. Figure 14 shows the same behavior with iron and zinc levels in water. That is, the iron and zinc concentrations were much higher with AQUATREAT AR-540 than with the AMPS/ Acrylate copolymer. This helps to confirm that the high phosphate levels shown in Figure 13 came from old deposits. Table II shows that the old system deposits do, in fact, contain substantial levels of iron, zinc and phosphate. Figure 14 shows excellent stabilization of zinc and iron with AQUATREAT AR-540 at the 8.6 operating pH of condenser water. High pH zinc stabilization is critical when zinc is used as part of a corrosion control program. Iron oxide dispersion and stabilization is important in helping to keep cooling water systems clean and free of settled deposits.

Figure 14: AQUATREAT AR-540 removes pre-existing iron and zinc.

Iron and zinc values

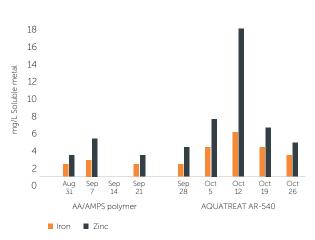


Figure 15 shows calculated phosphate/polymer ratios during both portions of this evaluation. Polymer concentrations used to calculate the phosphate/polymer ratios were estimated from measured molybdate values and the proportions of polymer and molybdate in this product. The feed ratio line in the graph (Figure 15) marks the 1:1 ratio at which phosphate and polymer were added to the system with chemical feed. The superior dispersive properties of AQUATREAT AR-540 compared to the AMPS/Acrylate copolymer are again apparent in this graph. The ratios during the AQUATREAT AR-540 portion of the evaluation confirm that the high phosphate levels came from the system and not simply from variations in chemical feed rate during the trial.

Figure 15: Both treatments were fed to maintain approximately 10 mg/L of polymer

Feed ratio



Summary

Both the AMPS/Acrylate copolymer and AQUATREAT AR-540 stabilized the phosphate added to the system with product feed. Important special benefits of AQUATREAT AR-540 that were demonstrated during this trial include:

- Dispersion and stabilization of pre-existing phosphate deposits
- Dispersion and stabilization of pre-existing zinc deposits
- Dispersion and stabilization of pre-existing iron deposits

Both the AMPS/Acrylate copolymer and AQUATREAT AR-540 have been previously shown to help stabilize soluble phosphate added with the chemical feed. The additional ability of AQUATREAT AR-540 to loosen pre-existing deposits and help to solubilize zinc and iron from these deposits is clearly demonstrated in this case history. These benefits make AQUATREAT AR-540 a powerful new component for use in phosphate and zinc-based alkaline cooling water treatment programs.

Evaluation—second year

In the first evaluation, pre-existing phosphate, zinc and iron deposits were redispersed and stabilized with AQUATREAT AR-540. Corrosion rates were at acceptable levels, but were somewhat high as deposits were removed from heat exchange surfaces. The second-year study was developed in the same cooling tower over an entire cooling season. Polymer feed was reduced by 20%, cycles were increased from 5-6 to 6-7, and zinc and iron deposits continued to be removed. By the end of the cooling season, corrosion rates were very low, and soluble iron and zinc were reduced to levels commensurate with those found in the feed water and expected from cycles of concentration. Figures 16-19 demonstrate the multifunctional efficacy of AQUATREAT AR-540.

System and operating conditions

- Pharmaceutical plant with tower providing comfort and process cooling—batch process and intermittent operations create ideal conditions for scaling
- Two-cell, 500-ton BAC cooling tower
- Two 250-ton York chillers
- Basin temperature = 80° F
- Temperature rise = 10° F
- pH 8.6
- LSI value is +1.27

Conclusions of second-year evaluation

- Mild steel corrosion was reduced to 1.5 mpy.
- Copper corrosion was reduced from 0.75 to 0.16.
- Zinc and iron deposits continued to be removed and at the end of the year were down to <0.2 and <0.05 respectively.
- Polymer-to-phosphate level was reduced to a ratio of 1:1.2 (20% less).
- Turbidity in the system was reduced from >60 NTU to about 20 NTU.
- Cycles were increased from 5–6 to about 6–7.
- System operated sludge-free.

Figure 16: Effective control of copper corrosion during the second-year trial.

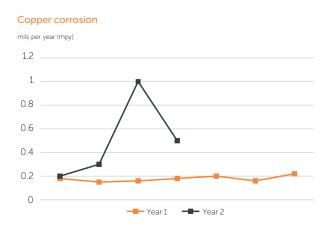


Figure 17: The effective control of mild steel corrosion during the second-year trial.

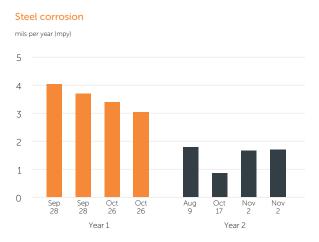


Figure 18: Initial high levels of both iron and zinc demonstrate AQUATREAT AR-540's ability to continue the removal of pre-existing deposits in year 2.



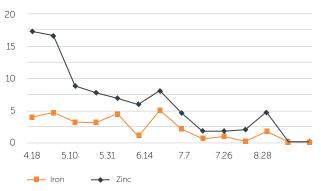
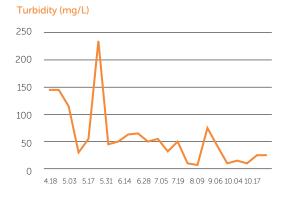


Figure 19: Initially high turbidity values show the dispersion of removed deposits in the system.



Storage and handling

AQUATREAT products are available in bulk, intermediate bulk and 55-gallon drums. The standard drum is fiber with 525 pounds net. Plastic drums are also available. AQUATREAT polymers have very low toxicity. Consult product MSDS for further information. Contact with the skin or eyes should be avoided. If an AQUATREAT product contacts the eyes, flush with water. If redness or sensitivity occurs and persists, consult a physician. AQUATREAT polymers should be shipped and stored in 304 stainless steel or better, fiberglass or plastic tanks. Certain phenolic linings are acceptable for use in drums and storage tanks. Mild steel, copper, brass and aluminum should not be used. The above materials of construction also apply to all pipes, valves and pumps used in the application or transport of AQUATREAT polymers.

Improve your business by using Aquatreat AR-540

Multifunctional polymer

- Calcium phosphate stabilization
- Calcium carbonate inhibition
- Zinc and iron control
- Removal of existing deposits

Thoroughly tested

- Broad lab evaluations
- Pilot tests in dynamic testing units
- Field evaluations
- Proven in industry

The security of Nouryon

- Proven history of quality, integrity, and innovation
- Trusted supplier to water treatment service companies around the globe



Contact us directly for detailed product information and sample requests.

USA and Canada Chicago, USA

T +1 800 906 9977

South America Itupeva, Brazil T +55 11 4591 8938

Central America and Caribbean Mexico City, Mexico T +52 55 5261 7895 **China** Shanghai, China T +86 21 2220 5000

> South East Asia Singapore T +65 6635 5183

India Mumbai, India T +91 22 6842 6700 Stenungsund, Sweden T +46 303 850 00

Europe

Middle East Dubai, United Arab Emirates T +971 (0) 4 2471500

Russia Moscow, Russia T +7 495 766 1606

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