Increased Versatility of Polyamide Fibers through the Use of Effect Additives

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Paper presented at the Seminar the 4th World Congress
POLYAMIDE 2003 The Polyamide Chain,
Zurich, June 2-4, 2003

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The maturity of the fiber markets forces producers to develop innovative products. Most additives used today in fibers are required to protect the polymer during manufacturing or to extend the lifetime of the fibers. This paper presents some of the latest developments in functionalizing Polyamide fibers through the use of appropriate effect additives. Effects such as antimicrobial activity and antistatic properties in Polyamide fibers and fabrics will be discussed.

ANTIMICROBIAL FOR POLYAMIDE FIBERS.

In recent years increasing public concern about hygiene has been driving consumer demand for antimicrobials in synthetic fibers. A variety of bacteria are known for their pathogenic relevance and their odor and stain formation. In order to address hygiene requirements antimicrobial additives like antibacteria, antialgae and antifungi have been introduced to the market. They are highly effective against a wide range of Gram-positive and Gram-negative bacteria by inhibiting their growth or blocking the food take up via photosynthesis or preventing the growth of a wide range of fungi.

Antibacteria

Antibacteria for the use in plastics should be highly effective on a broad spectrum of Gram-positive and Gram-negative bacteria. They have to have a very good tox profile and should be sufficiently compatible with the polymer matrix.

Table 1: PA 6.6 Fibers - Growth Inhibition Test
Use of Organic Antimicrobials

Samples	**Staphylococcus aureus** ATCC 9144		**Escherichia coli** NCTC 8196	
	ZI [mm]	**VR**	**ZI [mm]**	**VR**
Reference	0 / 0	0 / 0	0 / 0	0 / 0
with IRGAGUARD B 1000	10 / 11	4 / 4	4 / 5	4 / 4

Each test was performed twice and both results are given in the table.
Legend: **ZI** = zone of inhibition
VR = Vinson rating, for growth on the disc *
4 = no growth (good activity)
2 = weak growth (moderate activity)
0 = strong growth (no activity)
*Ref.: L.J. Vinson et al.: J. Pharm. Sci. 50, 827-830, 1961

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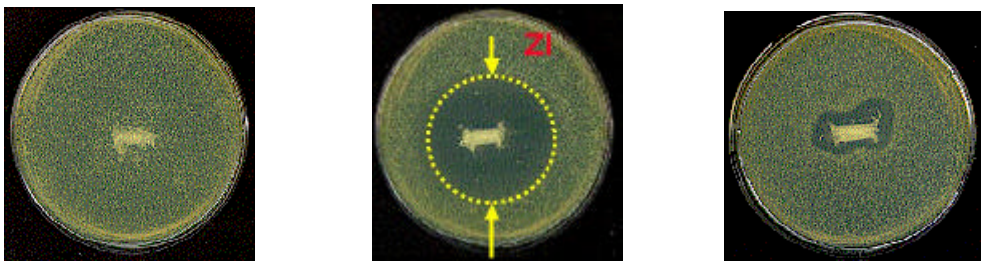
Table 1 shows the efficacy against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) on PA 6.6 socks compared to the Reference sample without antibacterium. Ciba® IRGAGUARD® B 1000 was incorporated in the PA 6.6 melt. Two tests have been performed. First, a PA 6.6 fabric was placed on an agar nutrition medium inoculated with bacteria. After 24 hours the result is the following: The dots around the control sample represent the colonies of the bacteria. The dark zone around the sample containing the IRGAGUARD B 1000 represents the zone of inhibition (Figure 1).

Figure 1: PA 6.6 Fibers - Growth Inhibition Test

Staphylococcus aureus (ATCC 914) | **Escherichia coli (NCTC 8196)**



without IRGAGUARD B 1000 | **with IRGAGUARD B 1000**

Often the zone of inhibition is small or even cannot be seen due to the non-migratory character of the antibacterium used. Anyway, the efficacy of the antibacterium is still there. Therefore a second method of determination of the efficacy is used, the Vinson rating. This method is a good qualitative judgment of the bacteria growth directly on the fibers. The rating goes from 0 to 4, whereas a Vinson rating of 4 means no bacteria growth.

Besides the use of organic compounds, antibacteria based on silver–ions are added. PA fibers are often spun at very high temperatures. Therefore the use of IRGAGUARD B 1000 based products can be limited due to the volatility of the product. For those applications the use of silver based antibacteria is recommended. These products have been optimized for bioavailability of the Silver-ions and to withstand the discoloration during sun light exposure, typical for standard Silver antimicrobials. Due to the non-migratory factor of the silver based antibacteria the agar diffusion test is not the test of choice. Therefore a test according to AATCC 100 measuring the Colony Forming Units (CFU) on socks is done.

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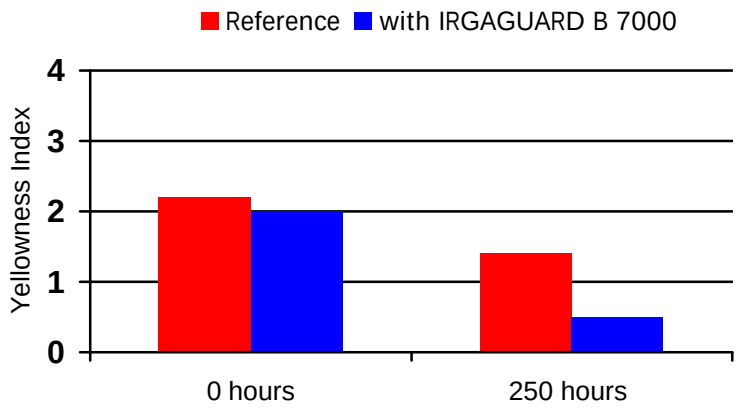
Table 2: PA 6 Fibers - Growth Inhibition Test
Use of Silver Based Antimicrobials

	Staphylococcus Aureus			*Klebsiella Pneumoniae*		
Additive	***0h***	***24h***	***Growth / Inibition***	***0h***	***24h***	***Growth / Inibition***
Reference	1.70E+06	4.10E+06	2.41	3.10E+06	6.10E+06	1.97
with IRGAGUARD B 7000		1.50E+02	-3.7E-05		<10	-1.64E-06

Fibers titer: 240/40 dpf
Determination of the bactericidal activity according to AATCC test method 100-1998 on socks
(Assessment of the antibacterial finishes on textile materials)

Table 2 shows an example of Ciba® IRGAGUARD® B 7000 performance in PA 6 fibers against two bacteria in comparison to a reference without any antibacterium. The amount of bacteria found back after 24 hours dropped close to zero in the sample containing IRGAGUARD B 7000. The sample not containing the antibacterium even shows growth with a factor of 2, a confirmation that the method works. As mentioned before, using silver-ions discoloration could be an issue when exposed to sunlight. Due to the specific design of IRGAGUARD B 7000 the color behavior of PA 6 containing this additive is at least similar to a non-antimicrobial product (Figure 2).

Figure 2: Light Stability of Antimicrobial PA 6 Fibers
Color Properties



Fibers titer: 240/40 dpf; Measurement on socks
Weathering conditions: 0.35 W/m^2 at 340nm, 63°C bst, no water spray

To get an extended life time of the PA 6 under sunlight similar stabilizer systems for light stabilization can be used in treated PA 6 as with untreated one (Figure 3).

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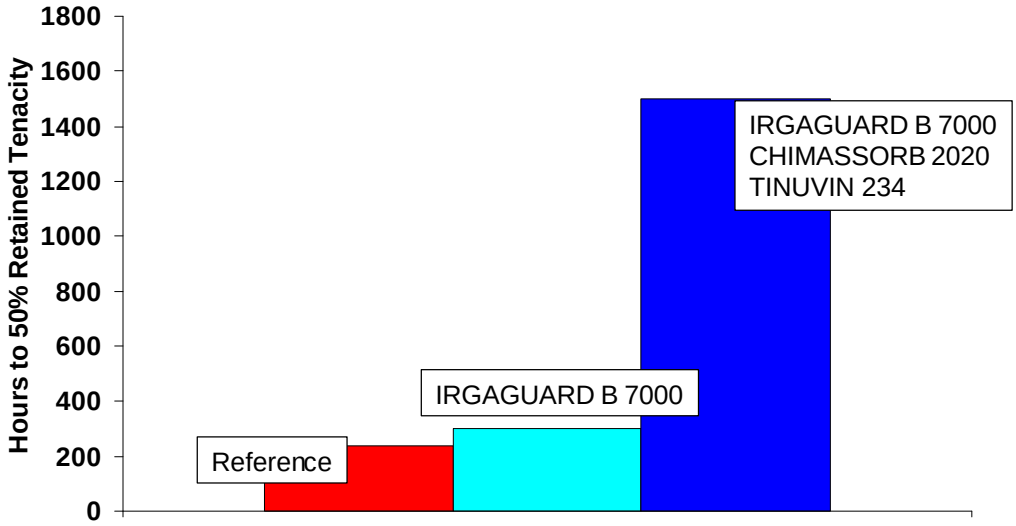
Figure 3: Light Stability of Antimicrobial PA 6 Fibers

Mechanical Properties



Fibers titer: 240/40 dpf; Measurement on socks
Weathering conditions: 0.35 W/m^2 at 340nm, 63°C bst, no water spray

Typical application fields for animicrobial products are fabrics like socks or sport ware, hospital supplies like mats and blankets or sanitary supplies like tooth brushes.

Antialgae

Algae and moss deteriorate the appearance of textiles fabrics such as shade cloth and awnings used outside. In some particular cases such as artificial grass it can even affect the functionality. Cleaning is not always feasible. Recently Ciba® IRGAGUARD® A 2000 has been launched as antialgae and antimoss for synthetic fibers. IRGAGUARD A 2000 is a highly specific inhibitor of photosynthesis and therefore controls very effectively the growth of algae and moss on the surface of synthetic fabrics. The optimum balance between substrate compatibility and migration rates provides efficacy over the useful life of the article.
An example of the efficacy of IRGAGUARD A 2000 in PA 6 fibers is shown in Figure 4.

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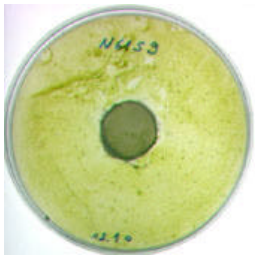
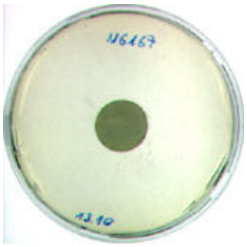
Figure 4: PA 6 Fibers – Algae Growth Inhibition Test
Use of Antialgae
Pseudokirchneriella subcapitata SAG No. 61.81
(= Selenastrum capricornutum ATCC 22662)



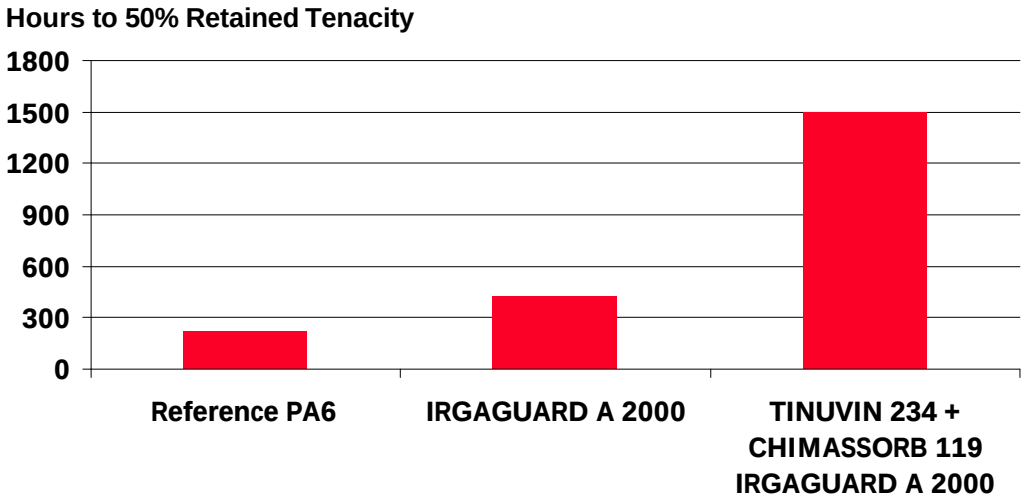
without IRGAGUARD A 2000



with IRGAGUARD A 2000

The algaecidal activity of PA 6 fibers containing IRGAGUARD A 2000 on the unicellular green algae species *Pseudokirchneriella subcapitata* (= *Selenastrum capricornutum*) was determined in a 7 days static test. Cultures of algae growing on agar plates were exposed to the treated and untreated fibers. The inhibition effect was determined qualitatively by visual assessment of the algae growth on the agar plates. Certain applications like fishing nets additionally require good light stability besides the efficacy against algae. Figure 5 indicates that IRGAGUARD A 2000 does not have a negative effect on the light stability of the fibers.

Figure 5: Light Stability of PA 6 Fibers containing Antialgae
Mechanical Properties



Fibers titer: 240/40 dpf; Measurement on socks
Weathering conditions: 0.35 W/m^2 at 340nm, 63°C bst, no water spray

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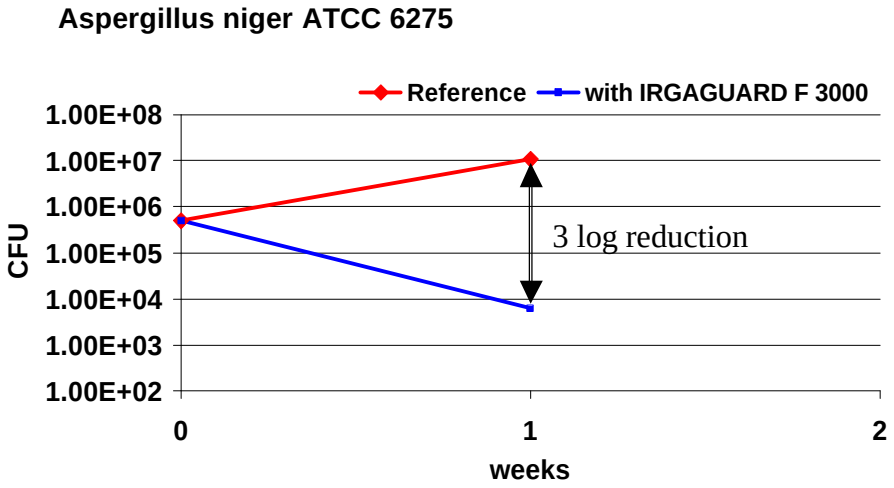
Antifungi

Humid conditions support fungi growth. Typical examples of fungi growth can be found e.g. under bathroom conditions. Besides the general hygiene aspects bad odor and also staining can often be observed. Polymeric products containing Ciba® IRGAGUARD® B F 3000 are capable to withstand the fungi growth.

Figure 6: PA 6 Fibers – Growth Inhibition Test
Use of Antifungi



Fibers titer: 240/40 dpf; Measurement on socks
Test according to AATCC 100-1998
CFU = Colony forming units

In Figure 6 the fungi reduction in treated PA 6 socks compared to a not treated sample is shown. After 1 week of exposure the amount of *Aspergillus niger* found back in the fungicidal sample dropped by 2 log CFU (Cell Forming Unit), whereas there was an increase of fungi in the untreated sample by 1 log CFU.

All these results show the excellent efficacy of antimicrobial additives incorporated in PA fibers. The combination of relatively good polymer compatibility and very high activity give the treated article long-term efficacy against bacteria, fungi and algae growth. These effect additives lead to improved hygiene, odor control, appearance and less maintenance in fiber applications, which allows a substantial product differentiation.

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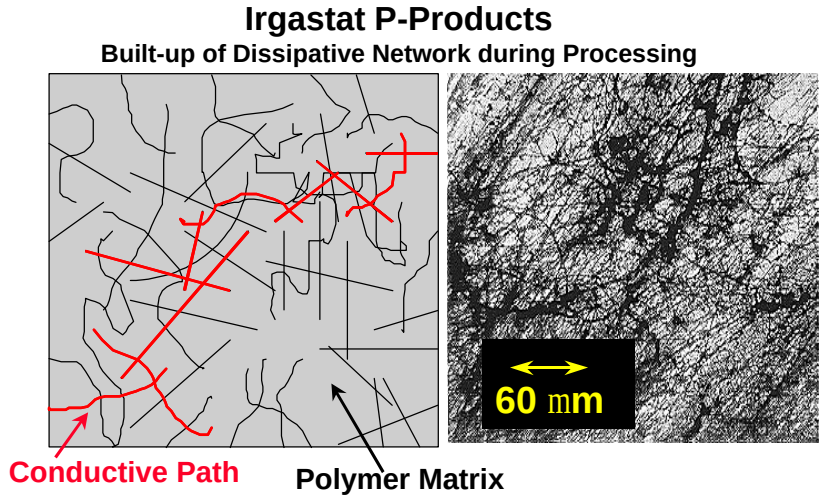
PERMANENT ANTISTATS FOR POLYAMIDE FIBERS.

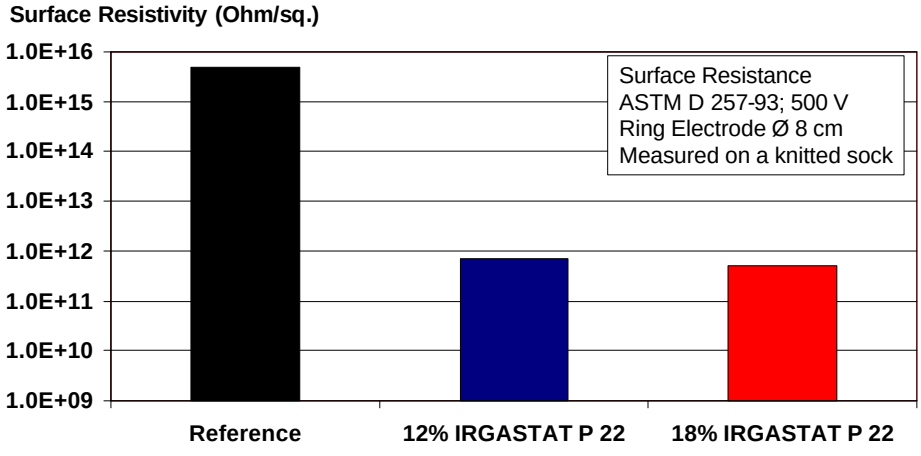
Static electricity is a natural phenomenon occurring during many industrial and commercial operations. Polymers with their insulating properties show very high surface resistivity (>10^{14} Ω/m^2) and are therefore strongly affected by the problem of static electricity.
On the basis of polyether block amides the permanent antistatic products Ciba® IRGASTAT® P were introduced to the industry. These are inherently static dissipative additives, working by formation of a dissipative network throughout the polymer (Figure 7).

Figure 7: PA Fibers – Antistatic Properties



This results in a permanent antistatic performance of the Polyamide fiber.
Different to conventional antistats, these new additives are less volatile and non migratory thus permanent. They show an immediate effect after processing. Due to the inherent static dissipative characteristics of the network, the polymer matrix shows antistatic effect at relative low humidity levels.

Figure 8: PA 66 Fibers – Antistatic Properties
Influence of the concentration of IRGASTAT P 22



Multifilaments 10dpf, measured at 50% r.h.

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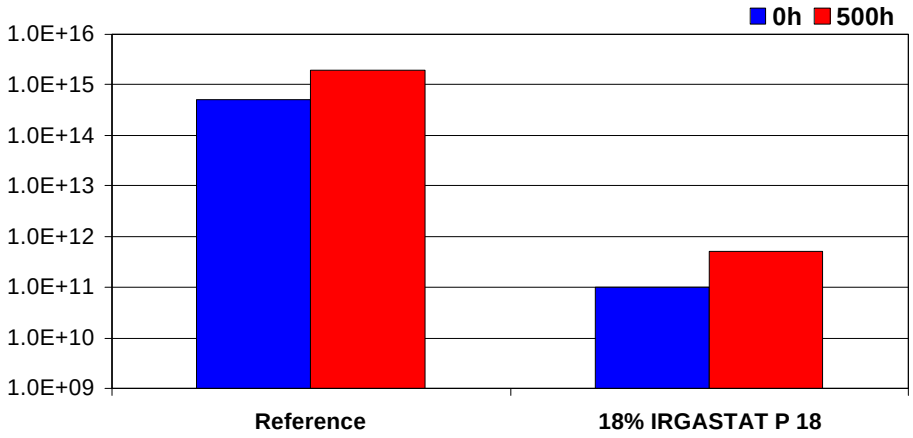
Figure 8 shows the surface resistivity related to different concentrations Ciba® IRGASTAT® P 22 in PA 6.6 fibers. The surface resistivity decreases with increased concentrations of antistatic agent. The fibers produced this way are biconstituent (2 components), therefore adjusting fiber-spinning conditions and concentration can optimize efficacy. Recommended use levels range from 8 to 15%.
In PA 6 the antistatic product of choice is Ciba® IRGASTAT® P18 in the concentration range of 12% to 18%.

Figure 9 : PA 6 Fibers – Antistatic Properties
Influence of the Artificial Weathering



Multifilaments 15dpf, measured at 50% r.h.
Weathering conditions: 0.35 W/m^2 at 340nm, 63°C bst, dry

Figure 9 shows the surface resistivity of a PA 6 containing 18% IRGASTAT P18 before and after artificial weathering at 50% relative humidity. Here again the positive antistatic effect is clearly visible. Additionally it can be seen that UV light is not negatively influencing the static dissipative performance of the samples
IRGASTAT P products open new fields for polyamide fibers, especially in applications requiring a durable effect or where low relative humidity can prevail. Typical applications could be electronical packaging, clean room applications or even carpets to reduce the dust pick up level.

CONCLUSIONS

Synthetic fibers can be functionalized through the use of well-selected additives. Traditionally, a lot of different effects like thermal stability, light stability or optical brightening are built into the fibers. These days also new effects such as antistatic and antimicrobial activity can be achieved. The data presented in this paper above are selected examples for antistatic, IRGASTAT P line, respectively antimicrobial effect additives, IRGAGUARD A for Antialgae, IRGAGUARD B for Antibacteria and IRGAGUARD F for Antifungi performance. In most cases, the right formulation of additives for the synthetic fibers have to be adjusted in order to fit the market needs. A good understanding of effects and the chemistry is necessary to make optimum

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recommendations for value added fibers. Our goal at Ciba Specialty Chemicals is to develop integrated additive solutions for synthetic fibers.

ACKNOWLEDGEMENTS

The developments represented in this paper are the result of immense work and effort by colleagues worldwide. The authors would like to thank all of them.

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