elements

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naphthalates from bp—expanding the use of polyesters

advances in ultraviolet protection

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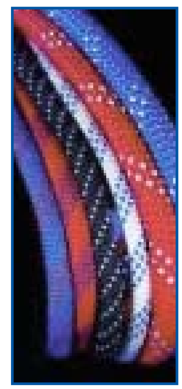

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advances in ultraviolet protection

BP's naphthalates add UV-protective properties

NDC's UV-blocking property has led to growth in applications requiring colorless, low-cost ultraviolet (UV) absorption. The fused ring structure enables it to function as a colorless, protective barrier against the harmful effects of UV radiation. This UV-blocking property has led to growth of NDC in applications such as beverage and personal care product packaging, protective screening films, sail cloth fiber, and as a stabilizer in sunscreens and cosmetics.

PEN homopolymer for ultimate barrier

PEN homopolymer resin blocks UV radiation at wavelengths substantially higher than many other common thermoplastic polymers. PEN is visibly transparent yet provides a highly effective UV-protective barrier that prohibits transmission of UV light up to 383 nm. Other optically transparent materials such as PET, polycarbonate or even glass do not effectively absorb UV radiation without the use of additives. (See Figure 1.)

Figure 1
UV absorption cut-off for plastics used in packaging

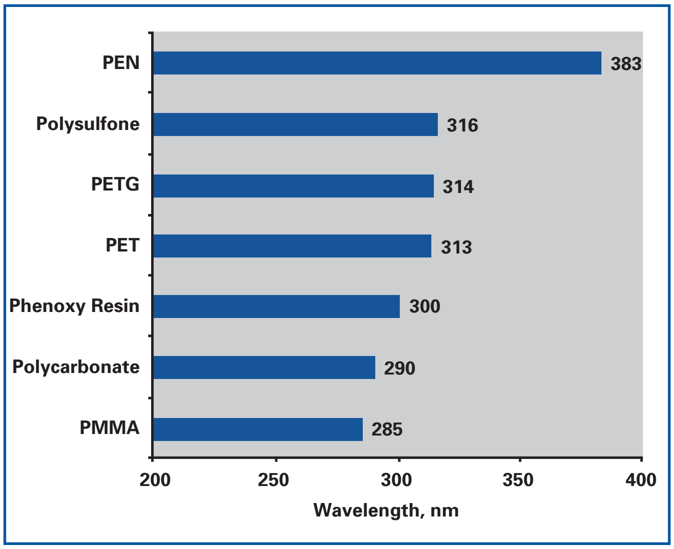
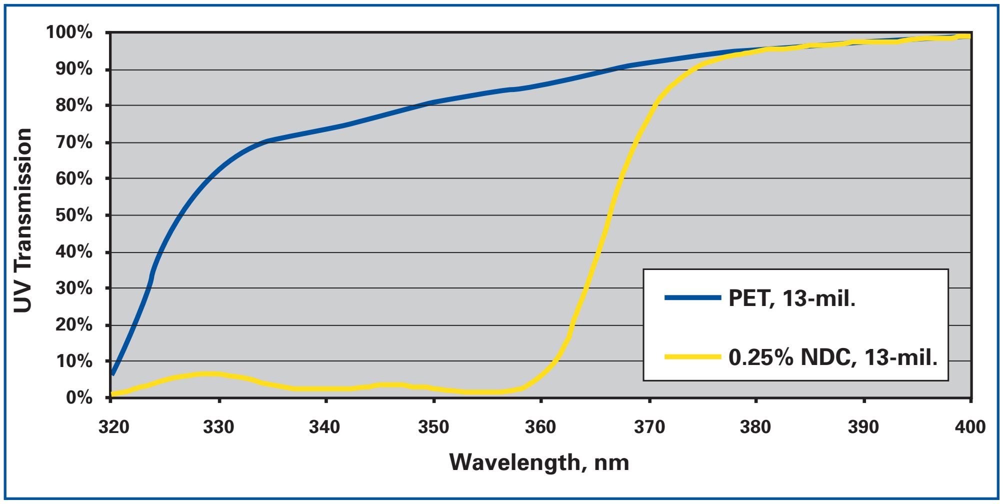


Figure 2
Ultraviolet light transmission of 13-mil. bottle sidewalls made from PETN-0.25 and PET



PETN copolymers for UV barrier

Naphthalates are ideally suited UV-barrier additives for PET. Their relatively high absorption coefficient means only small amounts are necessary to be effective. Studies indicate that naphthalate incorporation into PET at levels of less than 1 wt% can protect the color and flavor of packaged foods. (See Coca-Cola article.) The UV transmission spectra of PET versus 0.25% naphthalate PETN copolymer offer a stunning comparison of the UV-barrier protection that even low levels of NDC offer to polyester. (See Figure 2.)

The ability to block UV at low concentrations makes naphthalates a low-cost alternative to conventional UV-light-absorbing additives for polyester applications. (See Figure 3.) The raw material cost advantage with naphthalate additives can be four to five times less than conventional UV additives, when compared at 99 percent UV absorption and wavelengths less than 365 nm.

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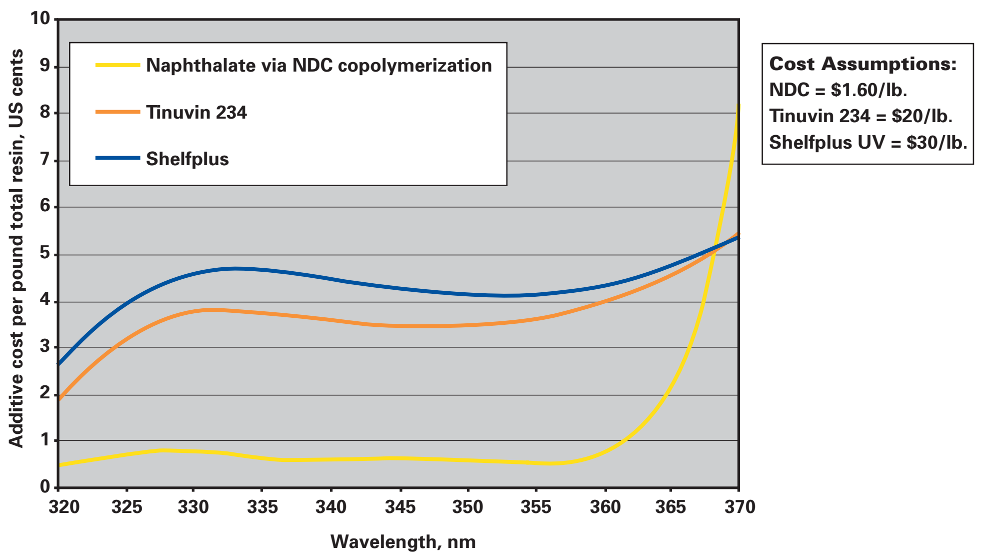
Figure 3
Raw material cost comparison of NDC vs. conventional UV protection for 99% UV absorption in a typical 13-mil. bottle sidewall



Naphthalate polyester preparation

NDC is colorless and can be directly incorporated into a polyester backbone so that the absorbing naphthalate species cannot migrate or bloom to the surface, unlike many commonly used UV-barrier additives. In addition, polyesters containing NDC are cleared for use in food contact and beverage applications by the FDA.

Naphthalate concentrations of 0.25–1.0 wt% are typical for UV-barrier polyester packaging. These naphthalate-containing PET resins can be prepared in existing PET polymerization or extrusion equipment using a variety of conventional methods, including: direct addition of NDC, PEN or PETN copolymer to the PET polymerization process; and blending PEN or PETN copolymer with PET in an extrusion process. Naphthalates can also be successfully incorporated into recycled PET by blending the recycled, repelletized PET flake (r-PET) with PENT-8 copolymer.

The UV-blocking capability of naphthalates adds to the expanding list of polyester performance improvements possible with NDC. BP is continuing to evaluate the UV-protective benefits of naphthalate-containing resins, and will report on new developments in future issues of *Elements*.

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advances in ultraviolet protection

Coca-Cola finds low-cost UV-barrier packaging

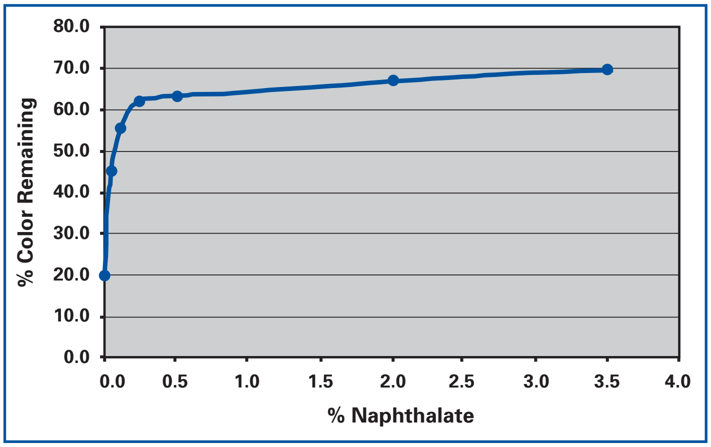
The Coca-Cola Company recently conducted studies showing that low levels of NDC incorporated into a PET bottle protect beverage color and flavor from UV light—at a cost significantly below that of traditional UV absorbers.

For this breakthrough, Coca-Cola questioned the basic assumptions of PET packaging. Historically, the assumption was that >90 percent absorbance at 390 nm is required for sufficient UV barrier. The visible spectrum begins at 400 nm, making it difficult to satisfy this UV-absorption criterion and remain colorless. And UV protection in PET comes at a high price—up to a 10 percent upcharge for traditional UV absorbers.

Pursuing a cost-effective alternative to traditional UV-protective additives, the company tested NDC as a copolymer additive in its PET bottles. NDC was chosen for its clarity, lack of color, UV absorbance, and the potential to be a low-cost solution. Additionally, polyesters containing NDC are cleared for use in food and beverage applications by the FDA.

A test beverage in an unprotected PET bottle retains no more than 20 percent of its yellow color after two weeks' equivalent sunlight exposure. This did not meet the company's standard criterion of success for UV protection, which is no less than 50 percent color retention after two weeks of sun exposure. Loss of color correlates well with flavor loss. With as little as 0.25 percent naphthalate in the PET, color retention exceeds 60 percent

Figure 1
Yellow color remaining after two weeks sun exposure vs. naphthalate content



after two weeks, well above the criterion for success. (See Figure 1.)

In a second study, the Coca-Cola Company evaluated a more sensitive product, a blue beverage aimed at the beach-going market. Unprotected, this product retains no more than 20 percent of its color after just 2 1/2 hours of midday summer sunlight in Atlanta. Again, 0.25 percent naphthalate in the PET bottle provides protection similar to that of traditional UV absorbers.

Unexposed PET Control | Exposed PETN-0.25 | Exposed PET Control

Naphthalate provides significant protection from sunlight to a blue beverage.

"The Coca-Cola Company sees step-change performance improvement in PET as a necessity for its continued growth in packaging applications," says Barnaby Wallace, global purchasing director, Plastic Packaging. "With smaller-sized bottles, and the need for improved shelf life, UV absorption is becoming an increasingly important aspect in a number of Coke markets."

Copolyesters of NDC are completely colorless and block UV effectively at wavelengths up to 365 nm—in contrast to PET, which is transparent to UV radiation above 310 nm. Says Wallace, "We decided to understand whether full protection was really needed for our products, or whether lower-cost additives would be effective."

In its studies, Coca-Cola concluded that low-level naphthalate addition to PET provides more-than-adequate UV-barrier protection for many of its UV-sensitive products. The ability of naphthalates to protect against UV radiation is similar to other commercial UV absorbers and is often significantly less expensive.

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advances in ultraviolet protection

NDC brings stability to sunscreens

C.P. Hall, a supplier of performance additives to the polymer and personal care industries, is taking advantage of the photochemical properties of NDC (dimethyl-2,6-naphthalene dicarboxylate) to stabilize avobenzone, a powerful UV filter used in sunscreens. The result is a lower-cost yet equally effective sunscreen.

Avobenzone is one of the most powerful UV filters available to sunscreen formulators. While most filters offer protection only to UVB, avobenzone protects from both forms of ultraviolet radiation: UVA and UVB. However, as it absorbs ultraviolet radiation, it loses power. Until recently, formulators overcame this by simply adding more avobenzone, an expensive solution. With C.P. Hall's HallBrite TQ, formulators can reduce the amount of avobenzone while ensuring the sunscreen's stability.

C.P. Hall bet on the FDA's approval of this full-spectrum filter, and began working on a stabilizing solution while it was in use only outside the United States. Craig Bonda, the company's technical director for Personal Care, says he knew that formulators around the world would be eager for a photostabilizer to use with avobenzone—especially one that also works as a solvent and an emollient.

"HallBrite TQ, now known as Corapan TQ, is a diethylhexyl ester of NDC, which we manufacture by terminating the NDC with 2-ethylhexanol," says Bonda. "The final compound, DEHN, is a liquid at room temperature that mixes easily with the oil phase of the sunscreen and is a good solvent for the solids in the sunscreen. That all makes it highly compatible with cosmetic chemistry."

The DEHN additive works by acting as a triplet quencher. As the chromophore avobenzone absorbs UV radiation, it becomes elevated to a triplet excited state. If this state persists, it is destructive to the avobenzone molecule. The DEHN takes on the energy from the avobenzone, which then returns to its ground state before the destructive chemical reaction can take place. As the acceptor, the DEHN molecule is elevated to a higher energy state, but this energy is released through heat and phosphorescence.

In creating an additive to stabilize avobenzone, Bonda chose NDC because it is the only photochemical that met his other criteria: nontoxic, cost-effective, and readily available. With the NDC-based additive, the avobenzone and other active ingredients in sunscreens can be cut in half. With the additive priced at about $6 a pound and the avobenzone at about $20 a pound, the savings are significant.

"Every major sunscreen formulator in Europe, Japan, Australia, and the U.S. has a development program underway looking at avobenzone," says Mark Miller, director of Marketing for the company's HallStar line of personal care additives. "The product makes good business sense for every one of them."

The product's solvency and refractive index also makes it a candidate for other personal care products, including clear gel systems such as antiperspirants and high-gloss lipsticks.

Recently, Haarmann & Reimer purchased the HallBrite TQ product, technology and intellectual property and will market it under the trade name Corapan TQ. C.P. Hall will continue to manufacture the product for Haarmann & Reimer and to market the photostabilizing technology in industrial markets.

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expanding applications

PEN barrier properties enhance Mitsubishi packaging film

By adding a layer of PEN to its PET film, Mitsubishi offers the food industry an ultra-high-barrier film that's ideal for the smaller packages used by today's busy consumers.

Known as Hostaphan® RHB, the coextruded PET/PEN film has high mechanical strength, excellent dimensional stability, high heat-resistance, and good printability. And with the enhanced surface quality from the PEN layer, Hostaphan RHB film offers better gas- and vapor-barrier performance after metallization or coating with a clear ceramic barrier layer.

Flexible packaging, using laminates of metallized Hostaphan RHB to heat sealant plies such as polyethylene, can replace metal cans. Heinz/Farley's in the UK developed a new packaging system—a laminate of PE and metallized RHB—for its baby milk powder. This packaging can achieve a freshness guarantee and shelf life of up to two years. The powder is packed into 75g sachets, and several sachets are packed together in an over-wrap of the same laminate.

In recognition of the unique performance of this product, the Association of Industrial Metallizers, Coaters and Laminators (AIMCAL) awarded Mitsubishi Hostaphan RHB 12 with its Technology of the Year Award in March 1999.

Heinz/Farley's (UK) new packaging system uses a laminate of PE and metallized RHB for its baby milk powder.

Providing the highest barrier performance

Metallized Hostaphan RHB laminates achieve an oxygen transmission rate of typically <0.2 $cm^3/m^2 \cdot d \cdot bar$ and comparable improvements in moisture barrier. High-barrier laminates of Hostaphan HB, achieved by laminating two plies of metallized RHB (metal to metal), are pushing oxygen transmission rates down into the aluminium foil range of <0.01 $cm^3/m^2 \cdot d \cdot bar$. (See Figure 1.) This measurable performance creates new opportunities—beyond those of metallized PET, the well-established standard for cost-effective, high-barrier flexible packaging.

Offering a clear choice

When transparent films are needed, PET films vacuum-coated with clear ceramics such as alumina (Al2O3) or silica (SiOx) can replace traditional materials such as PVdC-coated PET. Similar materials are becoming the first cost-effective, clear barrier packaging materials for foods highly sensitive to moisture.

The barrier performance of Hostaphan RHB attests to its suitability as a clear package for sensitive foods. The oxygen transmission rate of oxide-coated RHB is typically <1 $cm^3/m^2 \cdot d \cdot bar$, compared with a transmission rate of typically <2 $cm^3/m^2 \cdot d \cdot bar$ for oxide-coated PET laminates and >6 $cm^3/m^2 \cdot d \cdot bar$ for PVdC-coated PET laminates. The vapor transmission rate of oxide-coated Hostaphan RHB is comparably lower.

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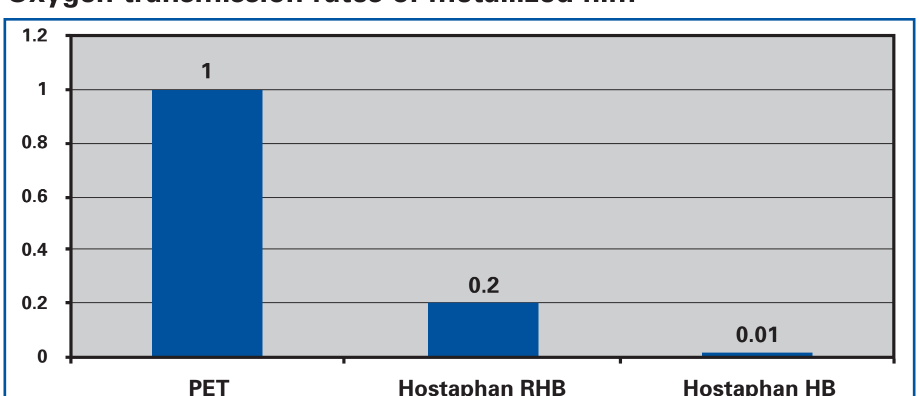
Figure 1
Oxygen transmission rates of metallized film



PEN surface properties provide unique performance

The film structure of Hostaphan RHB consists of a clear PET core with a surface layer containing PET resin and an antiblock filler, similar to standard PET film. The third layer is a clear PEN functional layer, oriented for optimal barrier performance.

The PET surface has the coefficient of friction needed for problem-free winding and normal machine performance, while the functional PEN surface is optimised to create an extremely smooth, undisturbed surface that results in a similarly regular barrier coating. (See Figure 2.)

Rexam Metallising of Thetford, UK, replaced a laminate of metallized PET and metallized polyethylene with a duplex of metallized Hostaphan RHB and polyethylene. (See Figure 3.) The improved runnability offered the end user a significant increase in packaging line speed.

For applications requiring both excellent oxygen- and water vapor-barrier performance, metallized or oxide-coated PEN-based Hostaphan RHB films provide the unique performance necessary to create a winning solution.

Figure 2
Structure of Hostaphan RHB

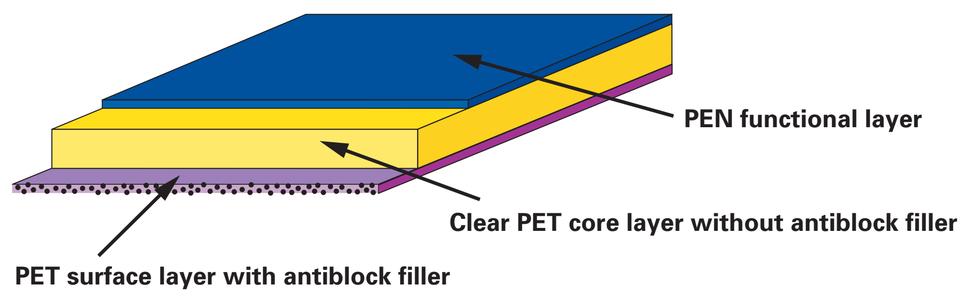
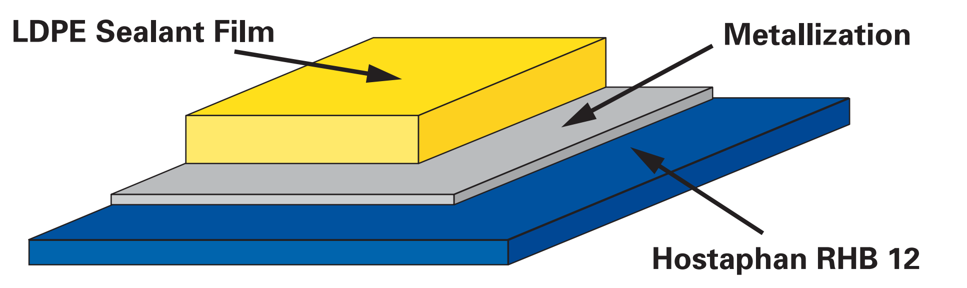


Figure 3
Structure of Rexam's high-barrier Hostaphan RHB laminate



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expanding applications

PEN fiber lends a steady hand to rescuers

In response to the need for a low-stretch, high-strength rescue rope, Sterling Rope introduced HTP™ Rescue rope, a high-tenacity polyester rope made with PEN fiber. The dimensional stability of HTP Rescue rope, with less than one percent stretch per 300-pound load, ensures steady support for rescue operations.

In contrast, the elongation and sagging characteristics of nylon rope can slow operations and put lives at risk. When ascending and accessing tall structures and buildings, rescuers can count on HTP Rescue rope to stay static when bearing the load of people and heavy objects.

PEN's resistance to UV light, chemicals and acid environments gives the rope greater durability in a variety of conditions. The rope excels in highline applications, where its low electrical conductivity makes it a safe choice. And because the rope does not absorb water, its weight remains constant.

The ropes are made with PenTex fiber (from Honeywell Performance Fibers), a high-performance PEN fiber that is also used in sailcloth, tire cordage and other applications. The advantages PEN brings to Sterling Rope's HTP Rescue rope apply equally well to other applications where tenacity, UV resistance, and non-conductance are needed. For example, the rope is ideal for sport climbing, window washing, and even for stretching African drum skins—and keeping them tight.

Sterling's HTP rescue ropes made from PEN fiber excel in lowering and extrication systems.

PEN fibers' high tensile strength supports many applications.

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expanding applications

PEN bottle protects volatile anesthetic

To minimize breakage, Abbott Laboratories' Abbott Hospital Product Division now packages its Ultane® anesthetic in PEN bottles instead of glass. The company chose PEN for its strength, clarity and gas impermeability.

Ultane, also known generically as sevoflurane, is a highly volatile liquid that induces general anesthesia when inhaled. Therefore, it's important that the container is both shatter-resistant and able to contain the product. PEN's exceptional strength, gas impermeability and chemical resistance make it ideal for packaging Ultane.

The new PEN container, a 250-mL amber-colored bottle, has now replaced the old glass container. Abbott manufactures the stretch-blow-molded bottle using resin supplied by M&G Polymers of Apple Grove, W.Va. The bottle is closed with a plain 24-400 black phenolic resin screw cap with a polypropylene insert. The new container is compatible with the same standard quick-fill and key-fill adapters used with the glass container.

Overall, the new PEN bottle has maintained the quality of the packaged product and helped simplify distribution and associated costs. With the bottle's lighter weight, shipping costs are reduced. Most importantly, breakage reports and replacement costs are now significantly lower.

plant news

BP's Decatur plant sets safety record

BP's Decatur, Ala., plant recently achieved 14 million hours without a "days-away-from-work" case. According to Danny Wallace, Decatur Works general manager, this record-breaking achievement is representative of the plant's growing "safety as a value" culture.

"We have a culture that encourages people to report incidents, no matter how big or small, and no matter what the results might be," says Wallace. "Many proactive process changes led to this level of performance. We've learned a lot and have developed good procedures. This is an outstanding accomplishment."

High standards of environmental and social performance are essential to BP. BP has a unified system of HSE management that is applied at all operating sites throughout the world.

fyi

New NDC Web site available

BP recently created a Web site that offers basic information about naphthalate polyesters and the company's naphthalate products. At www.bpchemicals.com/naphthalates, customers can access information about:

- NDC and HNDA specifications,
- MSDS and safe handling information,
- naphthalate polymer performance properties,
- naphthalate end-use applications,
- regulatory and recycle status,
- sample availability, and
- resin suppliers.

Naphthalates enhance the performance of polymers used in applications ranging from rigid packaging, to data-storage film, to passenger car tires. BP has a long, successful track record of helping downstream customers develop and promote their naphthalate-based products. This new Web site provides a comprehensive summary of naphthalate products, applications and use.

Again, visit the Web site at www.bpchemicals.com/naphthalates.

elements glossary

Glossary of acronyms

DEHN - di(2-ethylhexyl)-2,6-naphthalene dicarboxylate

HNDA - hydrolyzed 2,6-naphthalene dicarboxylic acid

NDA - 2,6-naphthalene dicarboxylic acid

NDC - dimethyl-2,6-naphthalene dicarboxylate

PC - polycarbonate

PE - polyethylene

PEN - polyethylene naphthalate

PET - polyethylene terephthalate

PETG - glycol-modified polyethylene terephthalate

PET/I/N - polyethylene terephthalate-isophthalate-naphthalate copolyesters

PETNx - terephthalate-naphthalate polyester copolymers (x=% of naphthalate)

PMMA - poly(methyl methacrylate)

PTA - purified terephthalic acid

PVdC - polyvinylidene chloride

UV - ultraviolet

UVA - UV radiation from 320–400 nm

UVB - UV radiation from 290–320 nm

disclaimer