Additives for
Maintaining Value the

What's needed
depends entirely on
the type of resin,
where it comes from,
and what you want it
to do in its next life.

In the recycling trade, where brutal
economic pressures never let up, it's
easy to think of additives as an unnec-
ecessary compounding cost. So, even those
ingredients considered vital in virgin
resin formulations can seem like expen-
sive frills on the second pass through the
pelletizing line. Yet today's
recycling markets demand
reprocessed resins that
meet the same
quality stan-
dards as their
virgin coun-
terparts.

Additives may be the best way to keep
old resins acting and looking like new.
Some compounders already rely
on stabilizers, lubricants, impact modi-
fiers and other processing and perfor-
mance additives to raise recycle to a
new level of value—sometimes even
above that of the original material. At
the same time, additives can help offset
the recycle stream's lack of homo-
geney, bringing individual lots up to
a consistent quality standard.

MRC Polymers, for instance,
employs both these strategies. The com-
pany reprocesses engineering resins
from industrial scrap and post-
consumer sources, producing
compounds that take on
virgin in the most
demanding auto-
motive and
electronics
applications.

“Additives are absolutely essential to our
business,” says George Staniulis, prod-
cut development manager. “We couldn't
live without them.” Straight recycled
polymer, he explains, simply would not
possess the physical properties or con-
sistency required by these premium
end-uses. Likewise, at Quantum Chem-
ical's Resource Recovery Facility in
Heath, Ohio, additives help preserve
quality in HDPE recycling. “Using
antioxidants is one way we differenti-
ate our resins from our competitors,” says
acting manager Bruce Perlson.
And as resins start to go through
the reuse cycle
Recycling
Second Time Around

more than once, additives will take on
greater importance. "It's likely that addi-
tives will make more of a difference for
more recyclers as recycled resins
become recycled themselves," predicts
Gerry Fishbeck, v.p. at recycling giant
Wellman Inc., Johnsonville, S.C.

Next to the mechanics of recycling
technology—sorting, cleaning, grinding,
and repelletizing—additives for repro-
cessing are still a relatively unexplored
frontier. "Much of the attention so far
has been on solving all these mechan-
ical engineering problems," says Peter
Solera, senior scientist at Ciba Additives.
Adds Wellman's Fishbeck,
"First, make sure the
recycle is contaminant-
free, and you're most of
the way there. Then,
additives can help you
go further."

Over the past year,
more and more additive
suppliers have recog-
nized the unique chem-
cal requirements of
reprocessed materials. The various
antioxidants, light stabilizers, impact
modifiers and other chemicals useful in
recycling may be basically the same as
those used with virgin, but blends
specifically proportioned for recycling
applications have emerged too. And
from recent applications, more infor-
mation has surfaced about the true ben-
efits of additives for reclaim.

RESTORING STABILITY

When polymer degradation poses
the key threat to physical property
maintenance, restabilization is the
prime solution. "By restabilizing, you
can protect properties and go back
into high-value applications," says
Joseph Puglisi, director of polymer
products at Ciba Additives. Depending
on the cause of polymer degradation
and intended end use, many recycled
thermoplastics can benefit from anti-
oxidants, light stabilizers or both.

Prevailing antioxidant strategy for
recycling many resins calls for hindered
phenolic and phosphite blends—or less
often, just one component. Because vir-
gin and regrind suffer from the same
degradation mechanisms, they both
benefit from the same stabilization
products, notes GE Specialty Chemicals
lead chemist Suzanne Dietz.

The required loadings can shift
upwards in recycling, though. For
example, an antioxidant typically used
at 220 ppm in a virgin polyolefin will
often be added at 1000-5000 ppm to
stabilize recycle, Dietz says. Optimum
loadings and ratios of dual components
vary widely because of such factors as
the feedstock's residual additive levels
and purity, Dietz points out. And indi-
vidual resins have inherently different
stabilization requirements, too.

For example, HDPE can suffer
from either crosslinking or polymer
chain scission during reprocessing,
both altering the molecular-weight dis-
tribution. According to Dietz, these
sorts of degradation manifest them-
selves as a shift in melt-flow index,
potentially causing processing prob-
lems for subsequent users and a drop

Impact modifiers enable polycarbonate scrap
from compact discs to find a second use in jewel
boxes that house them. Plus, they help overcome
metal and other contamination visible in the
close-up. (Photo: Amerifas)
in physical properties.

As a way to stave off HDPE melt-flow changes, whatever their direction, antioxidant blends can help. Multiple extrusion passes in GE’s labs show that HDPE’s melt flow remains far more consistent with stabilization. To maintain melt-flow consistency, a mixture of Ultranox 626 phosphite and Ultranox 276 hindered phenolic did the trick in 100% post-consumer HDPE (see Fig. 1). Dietz also notes that the phosphite inhibited color development, yielding a yellowness index of only -0.46 versus +9.04 for the unstabilized HDPE reclaim.

Work by Ciba’s newly formed Additives for Plastics Recycling Group in Switzerland shows similar improvements in recycled HDPE melt-flow consistency through the action of the company’s Irganox phenolics and Irgafos phosphites. And in polypropylene, where degradation generates polymer chain scission, the group has demonstrated that phosphite/phenolic blends can buoy the MFI through multiple extrusions. In one experiment, stabilized PP samples kept the same MFI after five extruder passes as an unstabilized reference sample retained after only two passes (see Fig. 2). At the same time, stabilization provided thermal stability far beyond that of the base material (Fig. 3).

And for both LDPE and HDPE, Quantum Chemical’s USI Div. has included BHT antioxidants in its Spectra-tech line of additive concentrates formulated specifically for recycling. PET can likewise gain from increased stabilization, though its individual requirements differ from polyolefins. Dietz says PET stabilization should rely on higher phosphate levels to prevent molecular-weight, or I.V., loss and maintain acceptable color (Fig. 4). Also, PET recycling may be especially application-dependent. Wellman's Fishbeck notes that PET reclaimed for fibers needs only the “traditional kind” of additives—such as optical brighteners and titanium dioxide pigment for delustering. But for nascent value-added PET recycle applications like thermoforming sheet, the additives requirements grow. “There’s no question that more additives are needed for thermoforming,” Fishbeck says. “Different grades of performance are required and these correspond to differing additives requirements.”

Stabilization’s benefits hold true for engineering resins as well; and here, rheological consistency takes on a special importance. “We have seen drops in viscosity correspond to drops in mechanical properties. Antioxidants inhibit this molecular-weight degradation,” says MRC’s Staniulis, citing experience with polycarbonate, TP polyesters, nylon and nylon alloys. Moreover, for most of MRC’s customers, consistent rhe-
ology is a non-negotiable prerequisite doing business. "Our resins can't vary more than 10% on viscosity versus shear rate from lot to lot," Staniulis notes. Some customers even demand rheology control to within three-sigma quality levels—a goal MRC says it meets.

Ciba's research work likewise demonstrates the potential of additives for saving physical properties of engineering resins (Fig. 5). By contrast, PVC reprocessing doesn't appear to create special stabilization or additives needs, according to suppliers. "Most compounds contain enough additives for two or three cycles," says Peggy Holsopple, technical service leader at Elf Atochem. If they don't, all the recycled compound needs is an infusion of the same sorts of additives used in the first run, according to Don Brilliant, technical director at Witco Polymer Additives.

**LET THERE BE LIGHT**

Heat—whether from processing or end use—is not the only enemy of recycled plastics. Applications, such as outdoor furniture, that expose resins to sunlight or other sources of uv radiation can also threaten a resin's longevity. A typical uv stabilization system today would combine a hindered-amine light stabilizer (HALS) with a uv absorber to safeguard color, according to Ciba's Puglisi.

One Ciba weatherability study found that addition of 1000 ppm (0.1%) of the company's Tinuvin 770 HALS enabled samples of HDPE from five-year-old milk crates to achieve the same weathering resistance as the original HDPE. Without restabilization, crack formation in 100% recycled HDPE took place at less than 2000 hr; the stabilized sample withstood more than 8000 hr crack-free. Tensile impact strength of the unstabilized recycle also fell far short of the mark set by the restabilized HDPE.

Responding to the need to combat different types of degradation—thermal and uv—simultaneously, some new additive systems combine antioxidants and light stabilizers in ratios optimized for recycling. Ciba recently introduced two such blends under the Recyclostab trade name. Already sold in Europe, these products should become available domestically in the third quarter, according to Puglisi. Both consist of hindered phenolics and phosphites, and one contains a light stabilizer. The Recyclostab 400 Series fits in applications needing long-term heat protection, especially for plastics from a mixed waste stream. And the Recyclostab 800 Series goes into applications demanding light stability as well.

Based on 15 years' experience in recycling, MA Polymers also sells additive packages optimized for reprocessing applications. The company can formulate its multicomponent antioxidant and light stabilization packages for injection molding, blow molding, sheet extrusion and thermoforming applications in a variety of resins.

**HAVING AN IMPACT**

Beyond using additives to restore or maintain physical properties at virgin levels, some compounders use a value-added strategy of upgrading recycled resins so they attain better physicals than the original. "We're not using any additives other than those with the ability to improve properties," says Michel Birrito, manager of resource recovery and recycling at Hoechst Celanese. She points to glass-fiber reinforcement and impact modifiers as the two most obvious choices to achieve these goals.

One supplier, AmeriHaas, reports that its Paraloid EXL impact modifiers have gained a new recycling application—turning polycarbonate compact-disc scrap into a resin suitable for making the "jewel boxes," or disc holders. Formerly made from a black HIPS tray and clear ABS cover, these PC compact disc holders now have displaced the earlier resins at one customer's plant. At 5-7% loading levels, the impact modifier more than doubled the strength of the PC while allowing it to accommodate the aluminum metalized layer from scrapped compact discs.

MRC Polymers, which also uses compact discs as part of its feedstock, makes extensive use of impact modifiers, according to Staniulis. In two automotive applications—a wheel cover and an interior console component—improved impact strength made the difference between MRC keeping and losing the business.

GE Specialty Chemicals recommends its Blendex ABS modifier resins to improve the impact strength and color hold in recycled ABS, SAN, PVC, and blends of these resins.
MORE COMPATIBLE

Produced from a Nylon/PPE alloy, the MRC wheel cover points to yet another route to upgrading recycled resins—combining dissimilar materials to get the necessary properties. MRC also sells a recycle-based PC/PET blend called Stanuloy. With blends, the key to success or failure may lie in use of compatibilizing additives. "The whole field of compatibilization technology is an area of fertile ground for recycling," notes Staniulis.

Although the technology remains highly proprietary, a number of different chemicals and polymers have shown effectiveness as compatibilizers (see PT, Feb. '89, p. 67). One of the newer products is AmeriHaas' Paraloid ExL-4100 Series of acrylic-imide copolymers for compatibilizing nylon/ABS and PC/nylon systems. The company's Paraloid PM-800 is an acrylic-polyolefin graft copolymer that can be applied to polyethylene-based blends. "We've seen success with PM-800 in PC/PE blends," says national sales representative Greg Torchiana.

Apart from engineered blends, compatibilizers may also help elevate the normally low physical properties of a commingled waste stream. A paper at this year's SPE ANTEC in New Orleans by A.A. Adewole and M.D. Wolfkowicz of Himont USA showed beneficial effects of Shell's Kraton FG1901X maleated MEBS copolymer on physical properties of a blend of PP industrial scrap with post-consumer HDPE. By varying Kraton levels between 1% and 7%, the authors achieved different balances of impact and elongational properties.

BASF Corp. has come up with three developmental compatibilizers for mixed-plastic recycle. These RCM polymeric blends products are designed to enhance properties of PS/PE, PS/PP, and ABS/PP blends (see PT, Feb. '93, p. 14).

In trying to make blends or commingled material easier to compound, processing aids can play a role. Struktol Co. reports that a recycling customer is using its TR 044 fatty-ester process aid to produce improved nylon/PET dispersions from regrind by means of viscosity adjustments.

The company also offers processing aids, such as TR 016, composed of a fatty acid metal salt and an amide. Because these have hydrogen sites available for bonding, explains product manager Don Hall, they can function both as flow aids and as coupling agents when blending recycled resins.

And Quantum notes that its Spectratech PM 11607 concentrate, containing a fluoropolymer processing aid, can help increase output rates and prevent melt fracture in recycled polyolefins.

LOOKING GOOD

Even recyclers using no other additives say they often use colorants to overcome appearance handicaps. Color comes in handy for masking the cosmetic effects of contamination, slight degradation, or the mottled appearance of commingled waste. "Even with stabilization, there's still a color shift, so you use color correctors," says MRC's Staniulis, citing blue tints to offset yellowness as one solution.

Quantum, for one, offers color concentrates specifically geared to recycling as part of the Spectratech line. According to market manager Ken Auer, an array of dark browns and blacks can uniformly color commingled resins at about 2.5% loadings. The company also offers recyclers a number of custom colors to boost appearance quality when black or brown won't do.

Foaming resins from commingled streams may be yet another way to improve both appearance and physical properties. Apart from potentially advantageous density reduction, foaming can eliminate warpage, improve impact strength, and impart more attractive surface, explains Auer. This way, lower-end applications like plastic lumber can gain aesthetic and functional value that they would otherwise lack. Auer adds that several Quantum recycling customers use concentrates of azo foaming agents.

NO CURE-ALL

Additives not only solve problems for recyclers, they may create some as well. Cost is the biggest. One recycler, for example, has seen times when the carbon black for masking mixed-color mottling has cost much as the recycled resin feedstock itself.

Non-uniformity of the recycle stream presents another key hurdle, despite the leveling effects of additives. "A dilemma we see is the additive control issue," explains Wellman's Fishbeck. "Recycling consistency is variable to begin with, so it's hard to anticipate what additive levels are needed." And Hoechst's Bitritto cautions that additive-induced compatibility problems can plague mixtures of diversely stabilized and modified reclaim—even in a single-resin feedstream. In such cases, she says Hoechst's best additive solution so far has been "adding more virgin."