

2.B Perfluorinated Copolymer Coatings for High-Power Laser Applications

Many common crystals for optical parametric processing, i.e., KDP, CDA, etc., are hygroscopic. Preserving their long-term stability and optical quality requires immersion in an index-matching liquid contained in some sort of cell.¹ Several drawbacks derive from this, not the least of which is cost, when up to 1-m beam and cell diameters must be considered for use in fusion-scale laser systems. Technical drawbacks exist as well; losses caused by transverse stimulated Raman scattering in the index-matching liquid, and photodissociation of the liquid by UV light are known to occur. Looking for a simple, cost-effective solution to protect KDP during in-air use, without incurring significant optical losses, led us to explore the benefits of the soluble perfluorinated polymers,² Teflon AF-1600 [66-mole-% dioxole (Bis-2, 2-trifluoromethyl-4, 5-difluoro-1, 3-dioxole) 34-mole-% tetrafluoroethylene, $n^D = 1.31$] and Teflon AF-2400 [84-mole-% dioxole (Bis-2, 2-trifluoromethyl-4, 5-difluoro-1, 3-dioxole) 16-mole-% tetrafluoroethylene, $n^D = 1.29$]. The refractive index of 1.29 (of the sodium-D line) is of interest because it is close to the value required for a simple, antireflective, quarter-wave layer on KDP. The refractive index of the copolymers decreases with increasing dioxole content and approaches the ideal refractive index of 1.24 for matching KDP. However, the solubility of the polymers also decreases with increasing dioxole content, precluding the use of the polydioxole or very-high-content dioxole copolymers. With this constraint and the corresponding refractive index mismatch, a quarter-wave layer of AF-1600 on KDP will, at best, reduce the single-surface Fresnel reflection loss of KDP to 0.4% at sodium D.

Whenever these Fresnel losses are acceptable, these perfluorinated coatings offer an attractive, low-cost approach to protecting optics. By now, several solvents exist, not all equally meritorious, in which the copolymers can be dissolved for spin deposition. Spatially uniform films result from an optimized combination of substrate diameter, spinning speed, solvent evaporation rate, solution viscosity, and solvent solubility. Both the tools needed to optimize the process and the required solvents are quite inexpensive when compared to the costs of mounting KDP in conventional cells.

The solvents tested were two pure perfluorinated polyethers, $C_{10}F_{22}O_2$ (Hostinert 130)³ and $C_{22}F_{46}O_6$ (Hostinert 272),³ and two mixtures of perfluoroalkylamines, (Fluorinert FC-40)⁴ and perfluorinated cyclic ethers (Fluorinert FC-75).⁴ Before use, the solvents were filtered to remove particulates larger than 1 μm . No further purification was attempted.

In this effort of coating planar KDP surfaces, 2-wt.% solutions of Teflon AF-1600 and Teflon AF-2400 were found optimal. Solutions with up to 10-wt.% concentration of Teflon AF-1600 were prepared, indicating that

highly viscous solutions can be made if desired. Films were cast on clean substrates under clean-room conditions. For curing and solvent removal, samples were kept at 100°C for 12 h. For KDP, much higher curing temperatures are not advisable.

Film thickness was derived from spectrophotometric scans covering the 300- to 1080-nm range. A typical scan in Fig. 48.20 plots differential absorbances (an uncoated reference sample of identical thickness was placed in the spectrophotometer reference arm) against wavelength. The transmission maxima near 350 nm and 1050 nm resulting from the single, coated surface are evident in Fig. 48.20. These two wavelengths represent the fundamental and third-harmonic wavelengths of neodymium lasers. The Teflon coating represented by Fig. 48.20 can therefore be used both as an input and exit-face coating on a KDP frequency-tripling unit.¹ The film used for Fig. 48.20 is chosen for illustrative purposes and does not constitute the best achievable, single-layer AR Teflon film on KDP. Here the single-surface reflectivity of KDP is reduced from 4% to 2.5%.

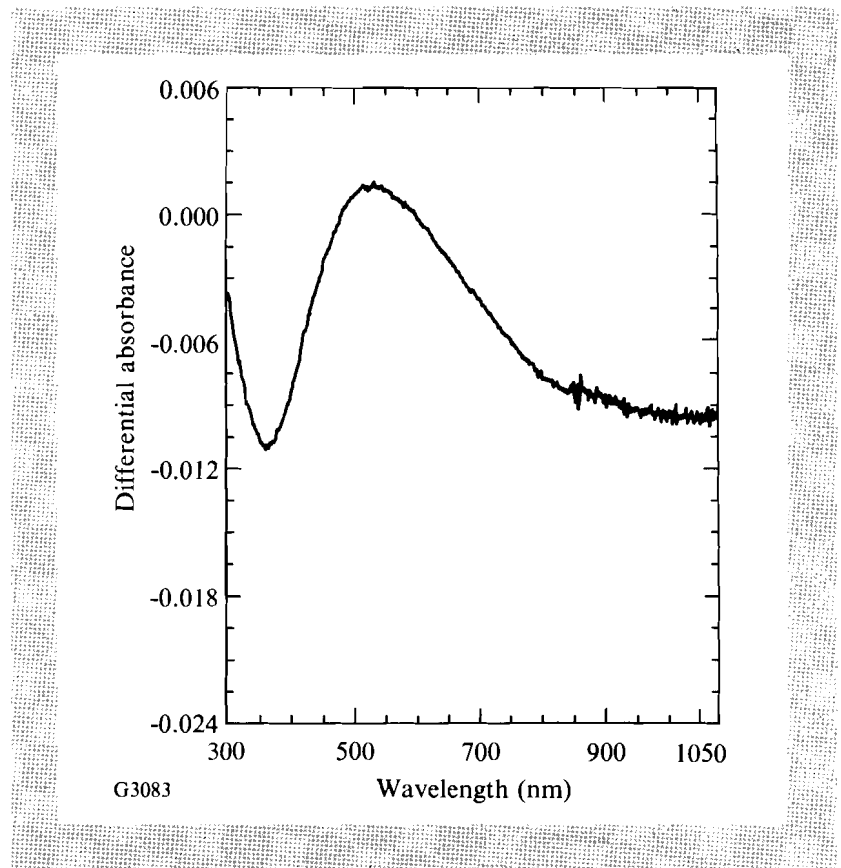


Fig. 48.20

Differential absorption scan of single-surface, Teflon AF-1600-coated KDP. An uncoated, similar-thickness KDP piece was placed in the spectrophotometer reference arm. The film reduced the reflectivity of the uncoated surface by 1.3% at 350 nm.

Optical survival strength is a pivotal criterion in screening materials for high-peak-power laser applications. In general, it is more difficult to meet peak-fluence requirements at shorter wavelengths. We report here 351-nm, 0.8-ns damage-threshold results from similar-thickness, AF-1600 films prepared on various substrates from different solvents. The damage-test substrates were conventionally polished, fused-silica disks and diamond-turned, flat KDP substrates (both 5-cm diam). The 351-nm irradiation spot size was 2 mm in diameter. These measurements yielded the results tabulated in Table 48.I. Damage is impurity driven in all but one solution-derived film. Only one solvent (Hostinert 272) is currently available in adequate purity to assure a film optical survival strength commensurate with multiple J/cm^2 applications. All other solvents leave residues in the films that cause sharp drops in damage threshold. This applies to solvents that were passed through 0.5- μm -pore filters. That low-volatility impurities are at fault in this situation can be shown by testing solutions directly. This is done using a prism geometry previously reported.⁵ Testing solutions, i.e., samples in which the impurities are highly dilute compared to films, invariably yields thresholds that are about one order-of-magnitude higher than those from films.

For the one solvent without significant impurities, a separate film-damage mechanism can be invoked. Both copolymers are fully saturated and are, as such, expected to exhibit intrinsically high damage thresholds.⁵ However, as polymerized, the copolymers contain some acyl fluoride end groups. These end groups are removed in a subsequent process step.⁶ The removal success varies somewhat from batch to batch. We tested damage thresholds for the presence of this π -conjugated group by preparing films from specially selected materials that were known to be either high or low in functional end-group density. The results in this case are very clear. Table 48.II shows a threshold improvement by a factor of 3 to 4, going from the Teflon version high in π -conjugated end-group density to the one 17 times lower in end-group density, all dissolved in Hostinert 272. For comparison, the result from a random-batch sample is included in Table 48.II as well. We have not explored which photochemical mechanism causes the *N*-on-1 threshold for this sample to be twice as high as the 1-on-1 threshold.

Table 48.II settles the issue of extrinsic, solvent-induced impurity damage: Hostinert 272 is the only known solvent that permits distinguishing the intrinsic, polymer functional group-derived damage from extrinsic effects. From a laser-systems design standpoint, Table 48.II provides bounds on the fluences at which a given system may safely operate, using coatings derived from standard, commercially available Teflon AF-1600. The single-shot threshold of $3.26 \text{ J}/\text{cm}^2$ and, even more so, the ramp-up, multiple-shot threshold of $7 \text{ J}/\text{cm}^2$ rank with the best alternative surface treatment methods.

Finally, we mention that more stringent antireflection requirements for this polymer sealant can be met by reverting to a two-component system. The original implementation of this concept⁷ used a different polymer whose

Table 48.I: Laser-damage thresholds (351 nm, 0.8 ns) of Teflon AF-1600 as a function of solvent and substrate. Film thickness is $\lambda/4$ at 351 nm.

Solvent	Substrate	1-on-1 J/cm ²	N-on-1 J/cm ²
FC-75	fused silica	1.89±0.02	2.36±0.61
25%/75% mixture of FC-40/FC-75	fused silica	<0.5	1.29±0.32
Hostinert 130	fused silica	1.90±0.1	1.83±0.60
Hostinert 130	KDP	1.06±0.02	1.50±0.14

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Table 48.II: Effect of functional end-group density on Teflon AF-1600* laser-damage thresholds (351 nm, 0.8 ns).

	1-on-1 J/cm ²	N-on-1 J/cm ²
High density	2.64±0.15	2.19±0.5
Random batch	3.26±0.20	7.1±1.0
Low density	7.75±1.49	8.39±1.51

*All samples prepared in Hostinert 272

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UV-laser-damage threshold made high-peak-power laser applications questionable. Two approaches are possible: one either seals the crystal surface with polymer first and deposits thereafter a porous sol-gel antireflection layer on top of the polymer, or one reverses the steps and seals the porous structure with the perfluorinated polymer as a barrier on top. We have investigated both approaches. One must note, however, that this layer reversal does not yield the same final transmittance in both cases. In practice, the latter approach is much simpler to implement; there, the Teflon layer is spin deposited on a conventionally prepared, sol-gel AR layer. In the reverse-order process, a challenge arises in the form of poor wettability of the Teflon surface. The key to proper wetting of the Teflon layer is the use of a fluorinated surfactant (FC-171)⁴ in the sol-gel solution at about 2% by weight concentration. Several other surfactants have been explored as well,

each one causing pH changes in the sol-gel solution that made control of the sol-gel porosity difficult. The two-component system yields, even without optimized deposition conditions having been established, transmittance through KDP in excess of 99.6% at 351 nm. Equally important, the optical survival strength at this wavelength is not reduced by the increased complexity of the two-component system.

We measured 0.8-ns damage thresholds for this system similar to those listed in Table 48.II: $6.6 \pm 0.2 \text{ J/cm}^2$ under 1-on-1 conditions, and $7.8 \pm 1.0 \text{ J/cm}^2$ under *N*-on-1 conditions. These results demonstrate that the perfluorinated copolymer Teflon AF-1600 is a superior medium for sealing hygroscopic frequency-conversion crystals, with the added advantage of providing a damage-resistant antireflection option. The polymer is easily processed and applied and is an inexpensive solution to large-crystal maintenance.

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