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1 Abstract

Polystyrene samples doped with commercially available coumarin derivatives were prepared and tested as wavelength shifters for plastic scintillation applications. Radiation damage studies were performed utilizing a ^{60}Co source. Transmittance and light yield measurements were recorded before and after irradiation (10 Mrad), and after annealing of the samples. All samples experienced losses in transmittance and light yield as a result of radiation-induced damage to the polymer and in some cases, the dopant. None of the coumarins examined in this study outperformed the commonly-used green wavelength shifter, K-27, after irradiation.

2 Keywords

Coumarins; Polystyrene; Plastic Scintillators; γ-irradiation; Radiation Damage.

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3 Introduction

Plastic scintillation detectors, which consist of a polymer matrix doped with fluorescent compounds, are noteworthy for their fast response and ease of manufacture. Their use in nuclear and high energy particle physics has spanned several decades. New applications for this type of detector have resulted from the development of scintillating plastic optical fibers (Bross, 1991). Several detectors have already been built, and many others are being designed, using various arrangements of polystyrene-based scintillating fibers.

A scintillating tile/fiber design is being used in a number of detector construction projects both at Fermilab (USA) and at CERN (Switzerland). This design consists of plastic scintillator plates embedded with a wavelength shifting (WLS) fiber that is spliced to a clear fiber (Foster *et al*, 1991). In order for this system to perform properly, the absorption spectrum of the WLS fiber must match the emission spectrum of the scintillating tile. Several of these projects have chosen SCSN38 (Kuraray Corp., Japan) for the scintillating tile and BCF91 (Bicron Corp., USA) or Y11 (Kuraray Corp., Japan) for the WLS fiber. These decisions were based on results from earlier radiation damage studies (Aota *et al.*, 1995). SCSN38 is a blue-emitting scintillator while both WLS fibers use K-27, a green-emitting compound, as dopant. K-27 has a decay time of approximately 12 ns which is long compared with that of most blue-emitting materials (2–3 ns). The lifetime of the green-emitting dopant is the main component affecting the speed of a scintillator tile/fiber calorimeter. To increase the speed of the calorimeter, green WLS fibers utilizing a dopant with a lifetime between 3 and 5 ns are required. However, currently available green WLS fibers exhibit decay times between 7 and 12 ns.

A number of groups are working on the development of new green-emitting WLS fibers with short decay times (Kauffman *et al*, 1995 and Gao *et al*, 1995). In a recent study performed at Fermilab, commercially available fluorescent compounds were tested in a polystyrene matrix. The spectroscopic characteristics of these compounds were determined after styrene polymerization, since this is an essential step in the manufacturing of the WLS fibers. The specifications of interest for this project were the following: λ_{abs}=400–450 nm, λ_{em}=450–550 nm, decay time faster than K-27 (ideally τ=3–7 ns), and a quantum efficiency of a minimum of 0.7 (current K-27 baseline). Large Stokes shift and low self-absorption were not important requirements since the optical path for the shifted light is small (typically 30 cm). A series of coumarin derivatives was found which approximately matched the requirements listed (Pla-Dalmau *et al*, 1995). Nonetheless, in most of the detector applications envisioned, the WLS fibers will be used in a high ionizing-radiation environment. Thus, before any substitute for K-27 can be selected, the results of a radiation damage study should be considered. The results of such a study are reported herein.

4 Experimental Section

Various coumarins meeting the absorption and fluorescence specifications listed above were purchased from Sigma, Exciton, Lambda Physics, and Eastman Kodak. Styrene was deinhibited by passing it through a column filled with alumina pellets (ALCOA, F-200) and was then purified by vacuum distillation. Glass polymerization tubes were treated for 10 minutes with a 30% solution of dichlorodimethylsilane in hexane in order to facilitate the removal of the plastic rods after polymerization. Styrene solutions were prepared containing a 0.02% (by weight) coumarin concentration and were degassed through repeated freeze-pump-thaw cycles. These solutions were polymerized in a silicone oil bath at 125 °C for 24 hours and at 140 °C for 48 hours. The bath temperature was then ramped down to 90 °C over 16 hours. After removal from the oil bath, the tubes were quenched in liquid nitrogen to cause a fast release of the plastic rods from the glass. The rods were cut and polished into discs of 2.2 cm diameter and 1 cm thick.

4.1 Light yield measurements

Light yield measurements of the coumarin-doped WLS samples were performed using a ^{106}Ru source. This β-source excited a sample of SCSN38 scintillator holding a WLS sample. The detector utilized for these measurements was a Hamamatsu photomultiplier tube with a green-extended bi-alkali photocathode. The pulse height spectra from these measurements were recorded with a LeCroy qVt operating in the charge mode. Light yield results reported herein have not been corrected for the quantum efficiency variations of the photomultiplier tube over the fluorescence distribution of the coumarin sample.

4.2 Irradiations

All samples were irradiated with a ^{60}Co source at the Phoenix Memorial Laboratory of the University of Michigan. They were irradiated in air to a total dose of 10 Mrad at a rate of approximately 1.8 Mrad/h. Transmittance spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. All transmittance measurements used an undoped and non-irradiated polystyrene sample as the reference.

5 Results and Discussion

The coumarin derivatives included in this radiation damage study are listed in Table 1. The initial selection was based on data from the literature in which coumarin samples were prepared in solution. The final series was chosen from the derivatives whose absorption and emission characteristics, after styrene polymerization, remained in the target region. The spectroscopic characteristics, in polystyrene, of the coumarins outlined in Table 1 have been published by Pla-Dalmau *et al* (1995). Samples doped with K-27 were also prepared and used as reference, for the current green WLS fibers are based on this dopant.

Transmittance measurements were performed before and immediately after an exposure to a dose of 10 Mrad. After irradiation, all samples showed signs of discoloration, from dark yellow to light brown. Within 10 days the samples presented signs of annealing. The radiation-induced color was slowly disappearing. A clear area was forming and moving inward from the edge of the disc. These phenomena have been observed in other irradiations of polystyrene-based scintillators (Johnson and Clough, 1993). The samples were measured at this stage and then placed in an oxygen atmosphere (160 psig) for two weeks to accelerate the annealing process. Although the samples were irradiated in air, they underwent annealing in oxygen atmosphere because the dose rate had been high enough that the oxygen diffusion rate was smaller than its consumption rate. The final results are similar to those of an irradiation under inert atmosphere, with the exception of the formation of oxidation products on the surface of the samples (Clough *et al*, 1991).

The discs had fully annealed after two weeks in oxygen, with the exception of those doped with C338, C498, C515, C519, C521 and C523. These samples were undergoing a second annealing process. These had lost the radiation-induced dark color, but the lighter color they were showing was also transitional. This lighter coloration was disappearing starting at the surface of the sample. Another front was forming as oxygen kept diffusing into the sample. This second annealing process had not been previously detected in the irradiation of standard plastic scintillators and wavelength shifters. Another set of measurements was recorded at this time, since the sample doped with K-27 was fully annealed.

Figures 1–3 show representative transmittance spectra at the four stages monitored. Figure 1 presents this set of data for a sample containing K-27, which is the current baseline. Figure 2 illustrates the transmittance changes for a C35-doped sample. This plot is representative of the coumarin-doped discs that underwent an annealing process similar to that of K-27. Figure 3 presents transmittance spectra for a C515-doped sample. C515 was a possible candidate to replace K-27 because of its shorter decay time and higher light yield. However, this sample is among the few that experienced a second annealing process. This fact suggests that this material requires a longer recovery period. Thus, its use in a detector would create a disadvantage with respect to K-27. Comparison of the results depicted in Figures 1–3 indicates that the K-27 sample has fewer radiation-induced changes in its transmittance spectra than the other two samples. In an attempt to better evaluate the radiation-induced damage to the transmission properties of the samples under test, the transmittance spectra before irradiation (A) and after oxygen annealing (D) were integrated. The integrated transmission losses were then calculated (Table 2). All the coumarin derivatives studied experienced transmission losses greater than K-27, and half of these compounds showed damage in transmission over 10%. Evidently, the compounds whose annealing process was still developing when this last measurement was recorded, have higher transmission losses. Therefore a final transmittance measurement was carried out on all the samples 18 months after irradiation, when all annealing had occurred. The percentage in transmission losses did not change for samples doped with K-27, C35, C485, C487, C490, C500, and C503. Small improvements in transmission (3–7% of values listed in Table 2) were observed for the remaining compounds, with the exception of C515 and C525. These two compounds showed an increase in transmission of 20% and

10%, respectively. Figure 4 illustrates this last transmittance measurement against transmittance data before irradiation and after oxygen annealing for K-27, C519, and C515.

Light yield measurements were performed before and after irradiation, and after the two-week oxygen annealing period. These data are presented in Table 2. Before irradiation, several samples such as C510, C521, and C522 showed similar or higher light yield than K-27. Immediately after irradiation, the light yield of all the samples decreased between 50% and 90% of its original value. This severe drop was caused by the absorption of the transient species created in the polymer during irradiation. As these species decay and the absorption decreases, the emission of the dopant is no longer partially reabsorbed by the polymer and can be detected in full (Bross and Pla-Dalmau, 1991). After irradiation and annealing, most of the coumarin samples recovered to a level that was approximately 50–60% of their original light output. But the sample doped with K-27 exhibited the highest light yield after recovery.

The losses in scintillation yield cannot be explained by the transmission losses observed. The light yield measurements were performed using a β-source that excited a blue-emitting scintillator (SCSN38) which, in turn, excited the WLS sample. Because the WLS sample had been irradiated, the polystyrene matrix was more absorptive. Therefore both the dopant and the polymer in the WLS sample competed for the blue-scintillator light. Fewer dopant molecules were excited by the scintillator light, and as a result, the light output of the WLS sample decreased. This problem in plastic scintillators is known as the hidden-absorption effect (Bross and Pla-Dalmau, 1991). Nevertheless, the possibility of radiation-induced dopant degradation was also considered. A structure-performance relationship was examined. In general terms, there appears to be a correlation between chemical structure and poor performance. Coumarin derivatives with a "quinolizine" fragment present higher transmission losses after irradiation. C515 must be noted as an exception, since it sustained considerable damage, but it does not include a "quinolizine" fragment in its structure. Figures 5 and 6 show representative structures of the coumarins studied. A more detailed analysis to support this correlation is not currently available.

6 Conclusions

Several coumarin derivatives exhibited the right spectroscopic characteristics and seemed possible substitutes to K-27 in the WLS fibers. However, the radiation damage study of these compounds indicated that they are not as resilient under radiation as K-27. The differences in transmission losses due to radiation-induced damage among the compounds tested are small, but a correlation with the structure of the compounds can be observed. An improvement in radiation stability may be achieved by preparing coumarin derivatives with the third and fourth positions blocked by substituents (Kauffman, 1993) and eliminating the "quinolizine" fragment.

7 Acknowledgements

We wish to thank R. Blackburn of the Phoenix Reactor Laboratory of the University of Michigan for performing all sample irradiations. We would like to extend our appreciation to the members of the Particle Detector Group for their technical support. This work was supported by the U.S. Department of Energy under contract No. DE-AC02-76CHO3000.

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9 Figure Captions

Figure 1. Transmittance spectra of a polystyrene sample doped with 0.02% K-27: before irradiation (A), immediately after 10 Mrad (B), 10 days after irradiation (C), and after oxygen annealing period (D).

Figure 2. Transmittance spectra of a polystyrene sample doped with 0.02% C35: before irradiation (A), immediately after 10 Mrad (B), 10 days after irradiation (C), and after oxygen annealing period (D).

Figure 3. Transmittance spectra of a polystyrene sample doped with 0.02% C515: before irradiation (A), immediately after 10 Mrad (B), 10 days after irradiation (C), and after oxygen annealing period (D).

Figure 4. Transmittance spectra of three polystyrene samples doped with 0.02% K-27, 0.02% C519, and 0.02% C515, respectively: before irradiation (A), after oxygen annealing period (B), and after 18 months (C).

Figure 5. Coumarin structures with a "quinolizine" fragment.

Figure 6. Coumarin structures without a "quinolizine" fragment.

Table 1. List of coumarin derivatives included in this study.

Coumarin	CAS Registry No.	Vendor	λ_{em}[a] (nm)
C153	53518-18-6	Lambda Physics	480
C314T	113869-06-0	Eastman Kodak	468
C338	62669-75-4	Eastman Kodak	472
C35[b]	41934-47-8	Sigma	460
C478	41175-45-5	Exciton	428
C480	41267-76-9	Exciton	428
C485	53518-14-2	Exciton	456
C487[c]	–	Exciton	430
C490	53518-15-3	Exciton	430
C498	87331-48-4	Exciton	470
C500	52840-38-7	Exciton	444
C503	55804-70-1	Exciton	446
C504	55804-66-5	Exciton	468
C510	87349-92-6	Exciton	484
C515	41044-12-6	Exciton	492
C519	55804-65-4	Exciton	488
C521	55804-67-6	Exciton	490
C522	53518-19-7	Exciton	472
C523	55804-68-7	Exciton	484
C525	87331-47-3	Exciton	518
C535	27425-55-4	Exciton	508
C540	38215-36-0	Exciton	514
C545	85642-11-1	Exciton	528

[a] Fluorescence wavelength. [b] C35 is equivalent to C481 from Exciton. [c] Neither the full name nor the CAS Registry number is available for this compound.

Table 2. Radiation Damage Studies.

Dopant[a]	Threshold[b] (nm)	T Loss[c] (%)	Light Yield[d] (%) Before Irradiation	After 10 Mrad	After Annealing
K-27	480	1	84	43	71
C153	470	10	83	18	45
C314T	460	14	89	24	56
C338[e]	460	17	88	24	53
C35	450	4	82	22	53
C478	420	14	55	6	28
C480	430	11	53	5	23
C485	450	2	90	22	23
C487	420	8	52	6	24
C490	420	8	44	8	35
C498[e]	470	13	92	23	49
C500	440	-	71	22	42
C503	440	5	74	17	42
C504	470	15	-	21	50
C510	480	12	100	22	54
C515[e]	480	19	84	18	47
C519[e]	490	12	84	25	55
C521[e]	490	12	89	28	54
C522	460	9	95	18	45
C523[e]	490	15	80	27	51
C525	520	15	69	18	49
C535	500	7	71	23	50
C540	510	8	76	30	56
C545	520	9	64	18	49

[a] Concentration of dopant in polystyrene is 0.02% by weight. [b] Absorption threshold for 1-cm samples. [c] Radiation-induced transmission losses calculated after oxygen annealing period. [d] Light yield results before irradiation are relative to C510. [e] Sample undergoes a second annealing process.

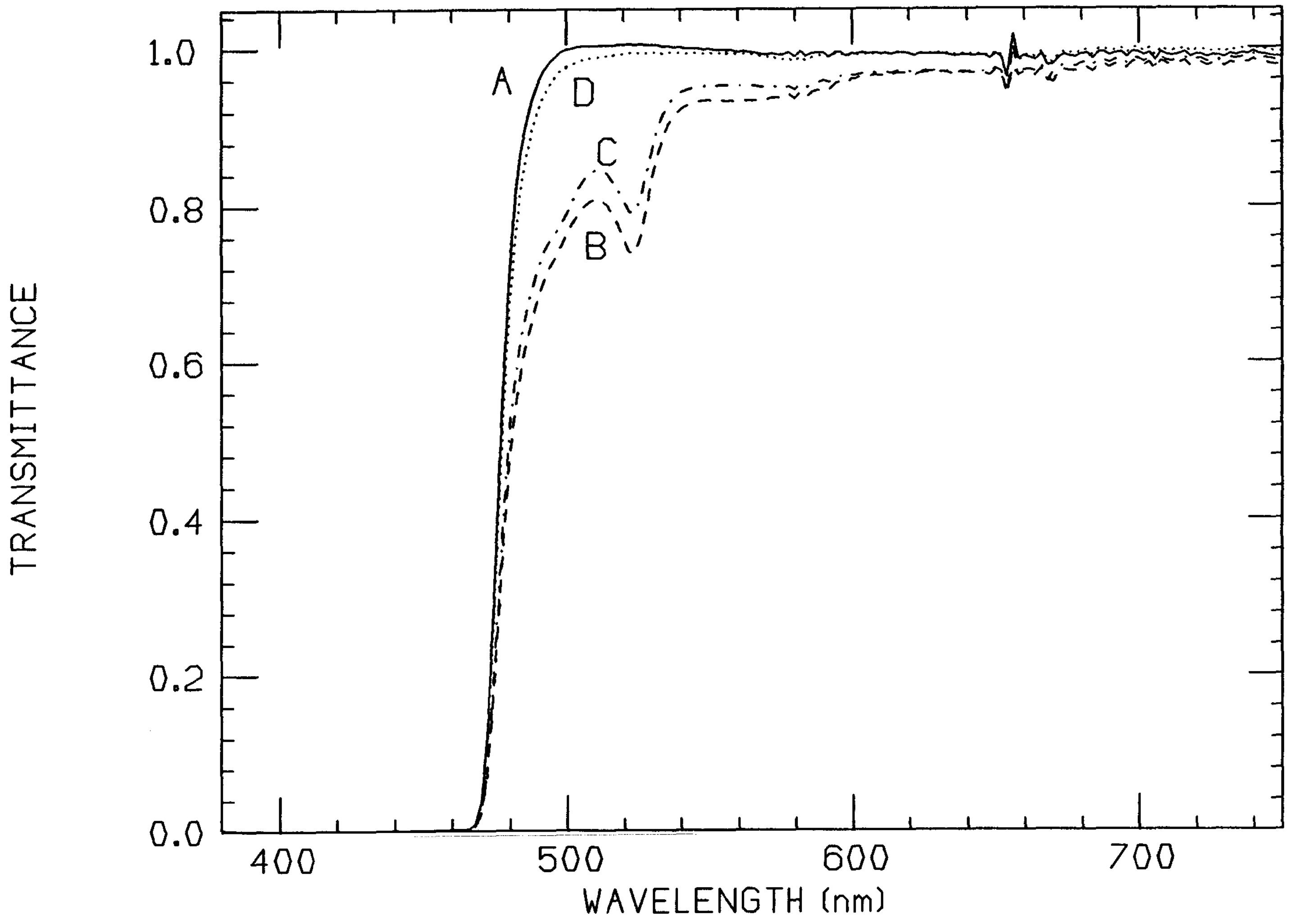
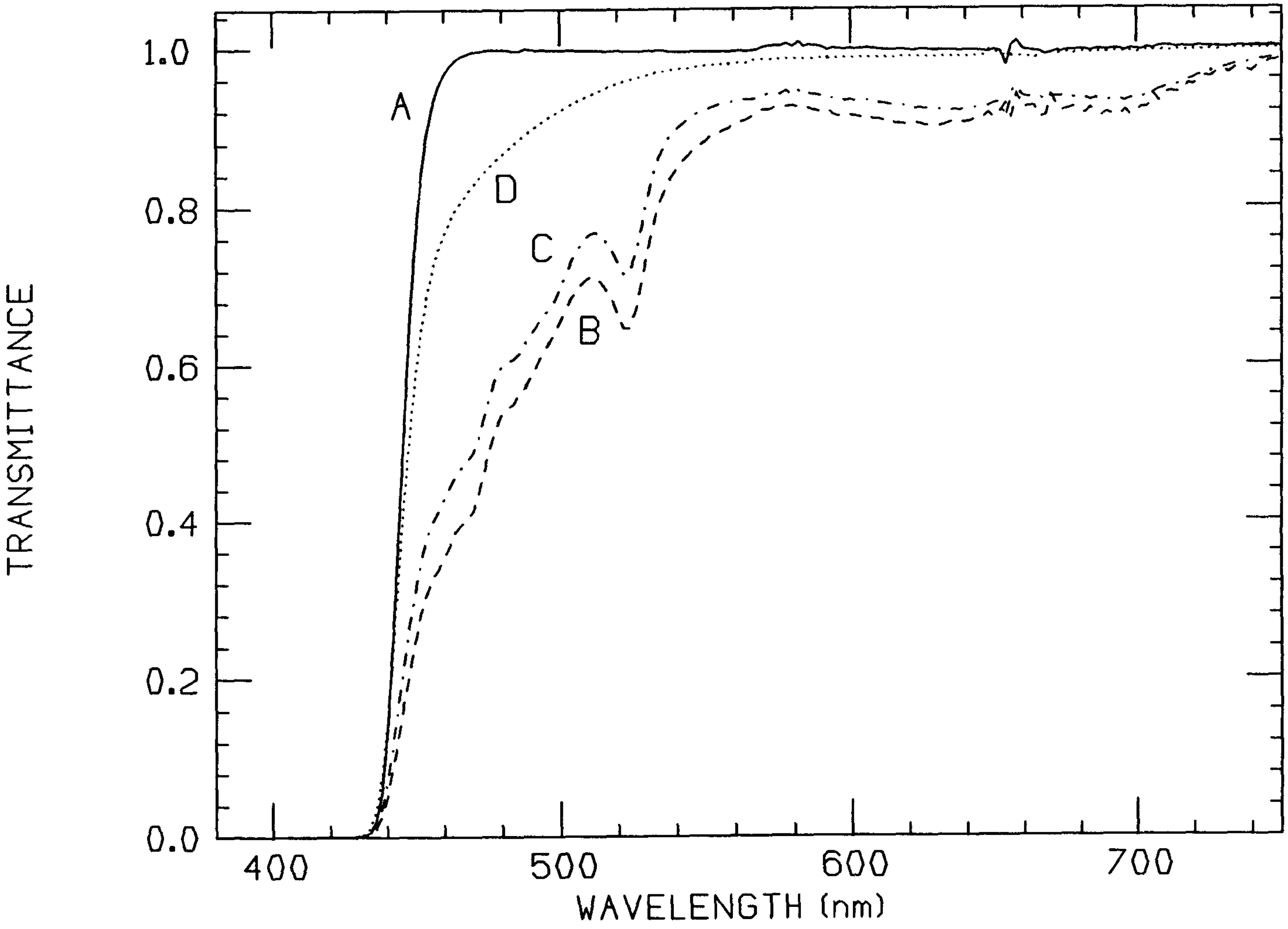

1.0
0.8
0.6
0.4
0.2
0.0
TRANSMITTANCE
400
500
600
700
WAVELENGTH (nm)
A
D
C
B

FIGURE 1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0.8
0.6
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TRANSMITTANCE
400
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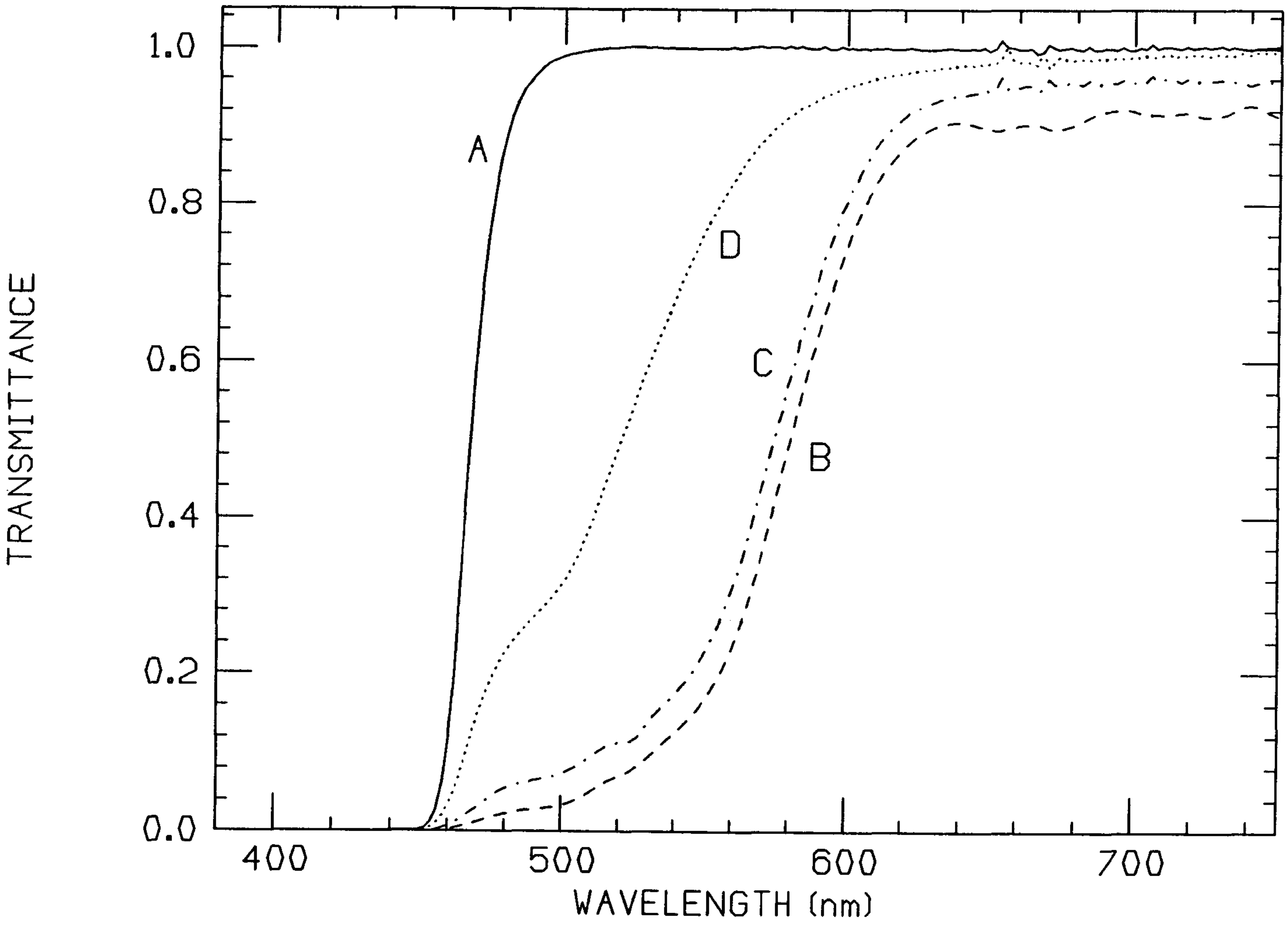
600
700
WAVELENGTH (nm)
A
D
C
B

FIGURE 2


1.0
0.8
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TRANSMITTANCE
400
500
600
700
WAVELENGTH (nm)
A
D
C
B

FIGURE 3

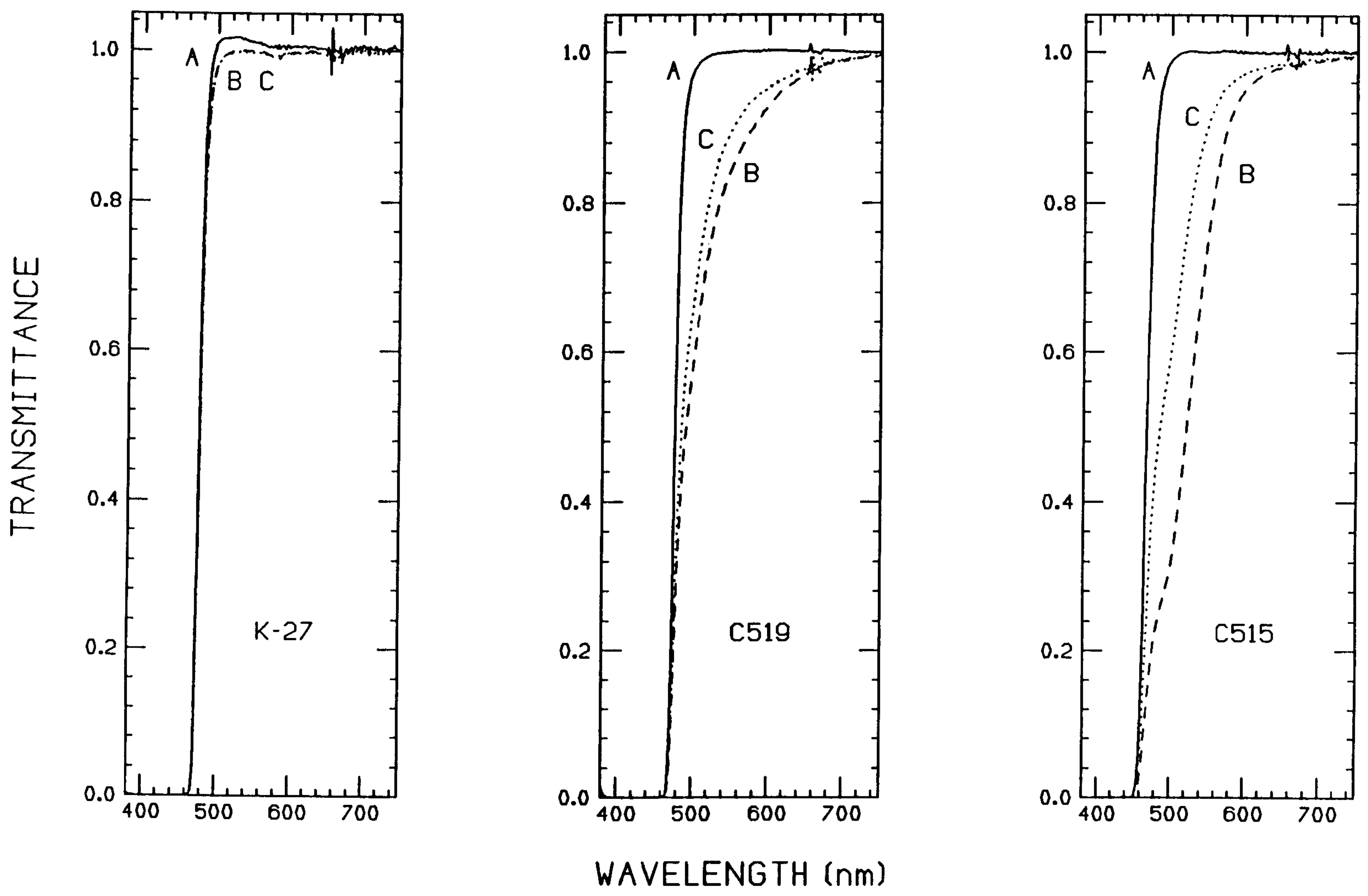
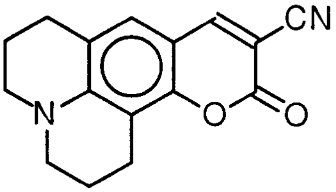
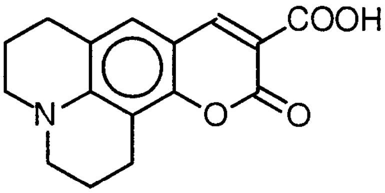

TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
A
B
C
K-27
C519
C515
400
500
600
700
WAVELENGTH (nm)

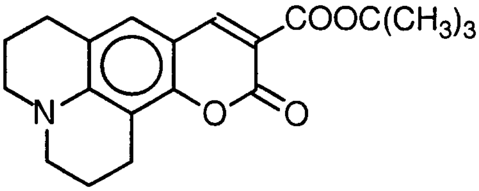
FIGURE 4



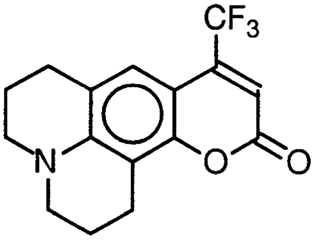
C523



C519

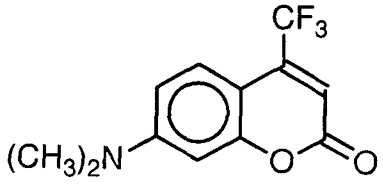


C338

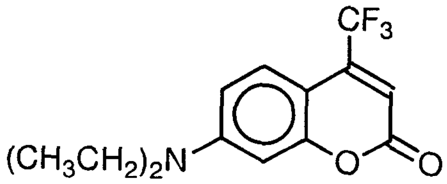


C153

FIGURE 5



C485



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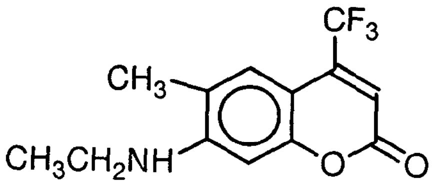
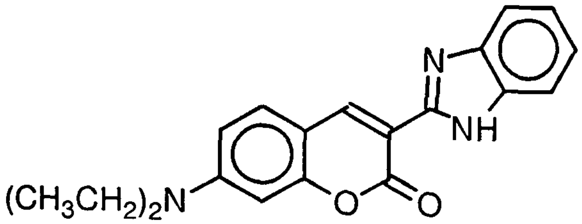


C503



C535

FIGURE 6