CHAPTER 9

New Developments in X-ray Sensitive Liquid Scintillators at EGG/EM*

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ABSTRACT

A summary of the liquid scintillators developed at EGG/EM SBO is presented. Among the characteristics presented are the emission spectra and efficiency values. All of the scintillation solutions mentioned herein have the potential for sensitivity enhancement to X-rays. One such successful red-emitting solution is L-735A-10T which shows a severalfold enhancement for a sample thickness of 6 mm, excited by 17-keV X-rays.

Other compounds containing heavy atoms such as tetramethylgermanium, tetraethyllead, and tetramethyllead were tested for possible heavy-atom quenching effects using high-energy electrons from a linac. The germanium compound showed no quenching effects, but both lead compounds exhibited considerable quenching of the fluorescence.

INTRODUCTION

At EG&G/Energy Measurements Inc., Santa Barbara Operations, work is in progress in the development of fast and efficient scintillators whose peak emissions are in the range from blue (350 nm) to red (840 nm). Some of the more successful formulations[1] are summarized in Table 1, along with the two commercially available plastic scintillators, BC-422 and BC-400.[2] Their spectral efficiencies are illustrated in Figure 1. The data in both table and figure were obtained by exciting the sample with a pulse of 16-MeV electrons whose FWHM is 50 psec.

In our work incorporating compounds with heavy atoms into scintillation solutions in order to increase their sensitivity to X-rays, we found that tetrabu-

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Table 1. Properties of Liquid Scintillators Developed at EGG/EM Santa Barbara Operations. Excitation by 50 ps FWHM Pulses of 16-MeV Electrons

Scintillator	Final Emitter	Conc. (*M*/l)	Shifter	Conc. (*M*/l)	Solvent	PRT (nsec)	FWHM (nsec)	Decay (nsec)	IRT (nsec)	% Eff.[a]	Peak Lambda (nm)
BC-400	—	—	—	—	—	0.9	3.1	2.3	9.4	2.31	420
BC-422	—	—	—	—	—	0.24	1.58	1.72	4.44	1.91	390
L-360	SG-180	0.035	—	—	PC	0.45	2.21	1.56	4.17	1.56	360
L-370	BHTP	0.14	—	—	PC	0.18	0.45	0.40	1.26	0.24	370
Liquid-A	TPB	0.022	PBD	0.027	PC	0.23	1.20	0.90	3.23	0.84	460
L-650A	DCM	0.03	C-480	0.10	BA	0.21	1.65	1.52	3.53	0.13	650
L-660	SR-640	0.002	C-540A	0.02	BA	2.66	14.45	12.09	26.30	0.27	640
L-735	LDS-722	0.02	C-540A	0.10	BN	0.21	1.54	1.27	2.77	0.10	735
L-841	LDS-821	0.005	Rh-610P	0.10	BA	0.52	1.88	1.37	3.99	0.04	850

[a]Refers to the ratio of the optical energy out vs the energy absorbed.

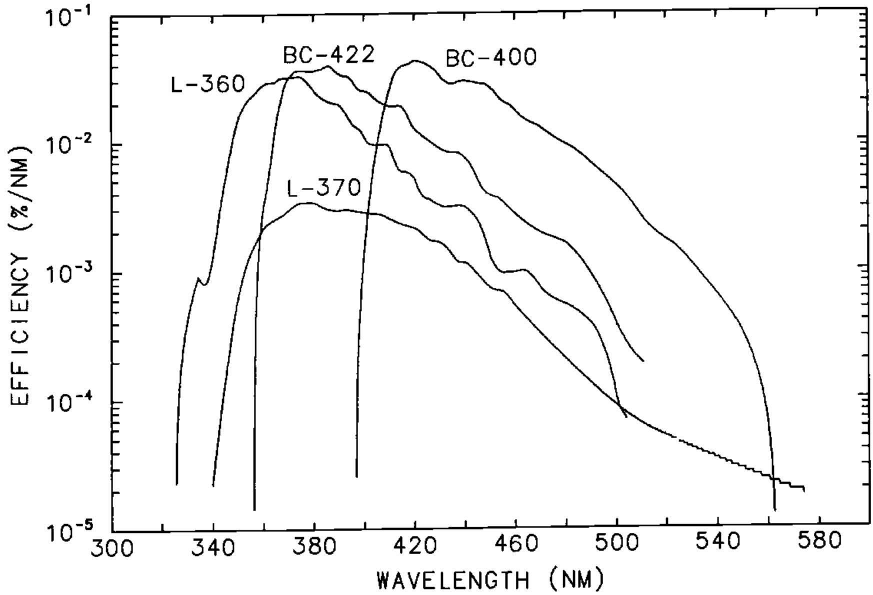

Figure 1a. Absolute scintillation efficiencies vs wavelength for liquid scintillators developed at EGG/EM Santa Barbara Operations.

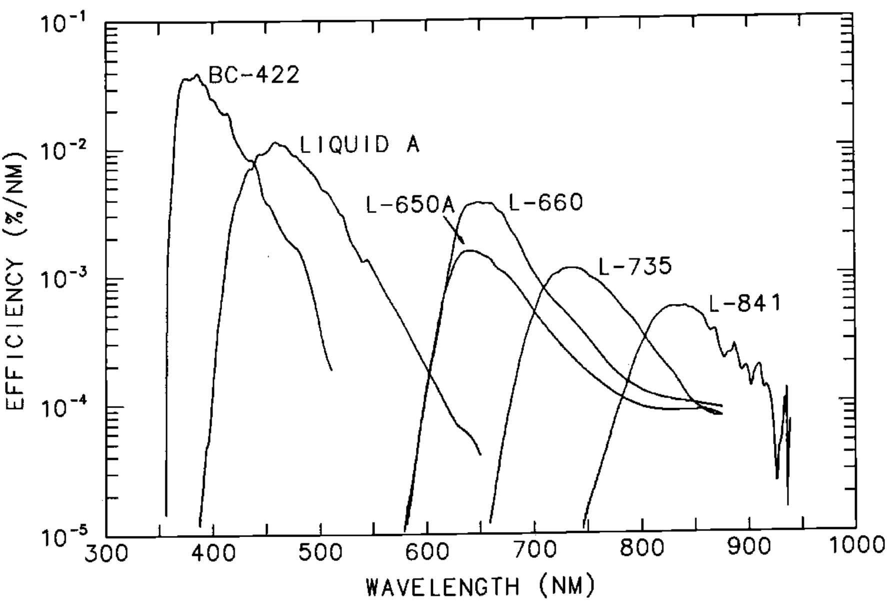

Figure 1b.

tyltin (TBSN) and tetramethyltin (TMSN) would not affect the scintillation properties except for a dilution factor.[3,4] The butyl and methyl groups are effective in isolating the heavy atoms from quenching the excited scintillator molecules. Thus TMSN, because of its higher percentage of tin, is deemed the more useful of the two compounds. Tin-loaded modifications of all the liquid scintillators listed in Table 1 have been successfully prepared.

Tin additives are particularly effective for X-rays in the energy range from about 10 to 100 keV; the K absorption edge for tin is at 29 keV. For lower energies, a lighter additive such as germanium, with a K edge at 11 keV, should be a more efficient absorber; for higher energies something like lead with a K edge of 88 keV would be preferable. Three compounds, tetramethylgermanium (TMGE), tetraethyllead (TEPB), and tetramethyllead (TMPB) were investigated for possible fluorescence quenching based on emission intensity and decay time measurements at the linac.

A new, tin-loaded, 735 nm liquid, L-735A-10T, has been developed, and its enhanced sensitivity to 17 keV X-rays has been measured. This new solution has a measured index of refraction of 1.53 at 740 nm and an optical attenuation of about 50 cm at 740 nm which make it attractive for use in capillaries.

EXPERIMENTAL

The scintillation parameters, including light output, were measured by exciting the solutions with pulses from a linac. The experimental arrangement is shown in Figure 2. These parameters include: 10 to 90% pulse rise time, FWHM, decay time from 0.7 of maximum to 0.7/e, 10 to 90% integral rise time (IRT), and the relative peak and integral of the fluorescence pulse to a reference scintillator.

The solutions were tested in 1 cm-thick Suprasil spectrophotometer cells and were bubbled with argon for two minutes before use. The samples were excited by 6 MeV electron pulses whose FWHM was 50 psec. The emitted light was viewed at an angle of 135° to the direction of the linac beam, as seen in Figure 2. This was done to reduce the Cerenkov contribution to the signal. Light from the samples was focused onto a Varian VPM 221D microchannel plate (MCP) photomultiplier tube (PMT), whose gain was 10^4. The light passed through a 335 to 427 nm FWHM band-pass filter. These signals were then sampled by a Hewlett-Packard sampling system Model 141A, with a remote sampling head. The signals were digitized with a CAMAC ADC and averaged and recorded with a DEC PDP-11/34.

A modification was made on the red-emitting liquid scintillator, L-735, listed in Table 1. The new scintillation solution, L-735A-10T consists of 0.01 *M* LDS-722 as final emitter and 0.10 *M* C-540A as intermediate wavelength shifter in a solvent consisting of 90 vol% benzonitrile (BN) and 10 vol% TMSN. The LDS-722 concentration was lowered from 0.02 *M* in L-735 to 0.01 *M* in L-735A-10T, because the solubility of LDS-722 decreased when the

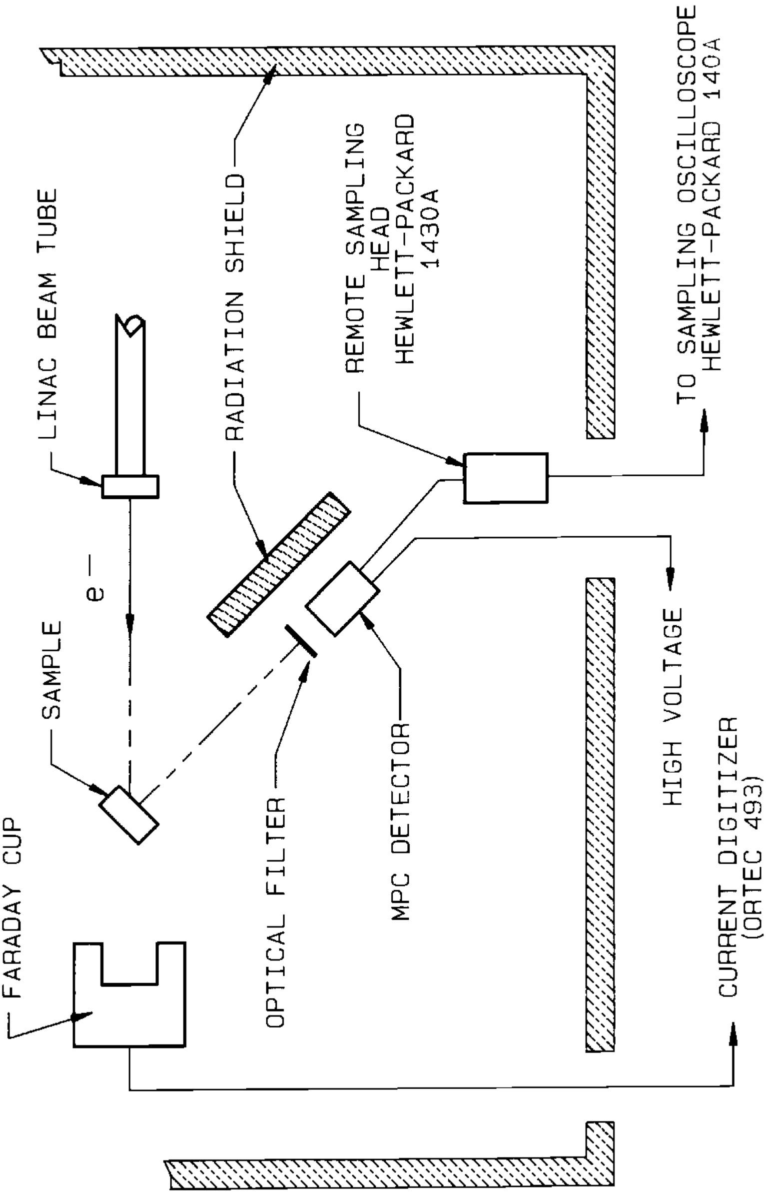

Figure 2. Schematic diagram of test configuration for the linac measurements.

TMSN was added. L-735A has the same dye concentrations as L-735A-10T but no TMSN.

The relative sensitivity of L-735A-10T to L-735A was measured by exposing samples to pulsed X-rays. These pulses were generated by 50 keV electrons, with a FWHM of 850 psec, incident on a molybdenum target as shown in Figure 3. Characteristic X-rays are superimposed on a bremsstrahlung spectrum that extends out to the 50 keV endpoint. The X-rays pass from the vacuum through a 5 m-thick beryllium window and are then filtered by a 3 m molybdenum foil which selectively passes the characteristic X-rays. The X-ray spectrum was determined by placing a 2 atm Xe proportional counter at the same position as the cell. A sample of the resulting spectrum, with the system response unfolded, is shown in Figure 4.

The samples were contained in a cell 12.7 cm in diameter by 0.6 cm in thickness. The window facing the X-ray source was 0.2 mm-thick beryllium, and the one facing the detector was 3.2 mm-thick Spectrasil-B. During measurements the liquids were heated to 43°C, a temperature typical of that encountered under field conditions. The light was filtered with a 630 nm long-pass filter and was detected with an ITT F4129 MCP PMT. The photocathode has an S-20 extended red response. The tube was as close as possible to the Spectrasil window for efficient light collection, and the output was sampled and averaged using a Tektronix 7854 digitizing oscilloscope with an S-12 sampling plug-in and an S-4 sampling head. The sampled pulses were then integrated, and the relative sensitivities were determined from the ratio of the integrals.

All chemicals were used as received. The BN, PC, and TMSN were from Aldrich Chemical Co.. The chemical TMGE was supplied by Alfa Products. The laser dyes LDS-722 and Coumarin 540A were from Exciton Chemical Company, Inc.. The compounds TMPB and TEPB were contributed by Ethyl Corp..

RESULTS

Tetramethylgermanium

As can be seen from the data in Table 2, the addition of TMGE had no measurable effect on the decay time of the 4,4″-di-(5-tridecyl)-p-terphenyl, SG-180,[5] in pseudocumene (PC). The relative pulse integral values actually decreased somewhat less than would have been expected from simple dilution of the PC by addition of the TMGE. Thus there is no evidence of any quenching by the TMGE. It was found previously that when TMSN or TBSN was added, the emission intensity also decreased in proportion only to dilution of the PC.[3,4]

One problem with TMGE is its high volatility: it boils at 43°C. Tetraethylgermanium has a higher boiling point, 163°C, but it contains a lower percent-

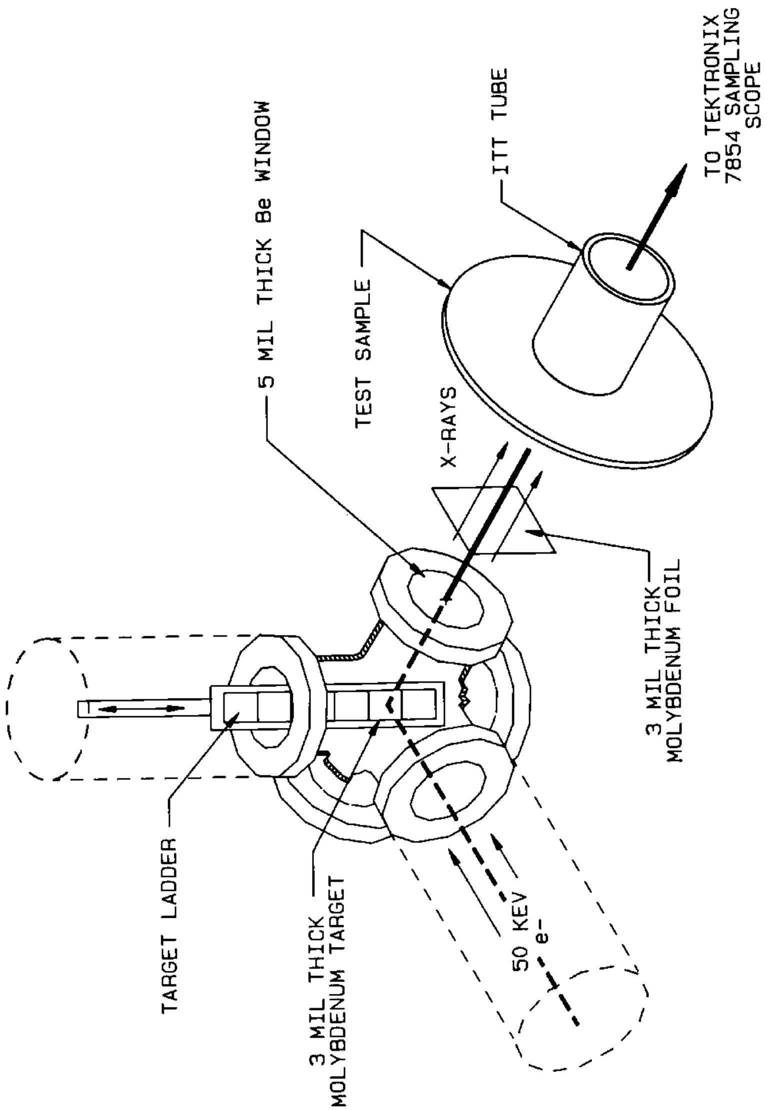

Figure 3. Experimental setup for the relative X-ray sensitivity measurements.

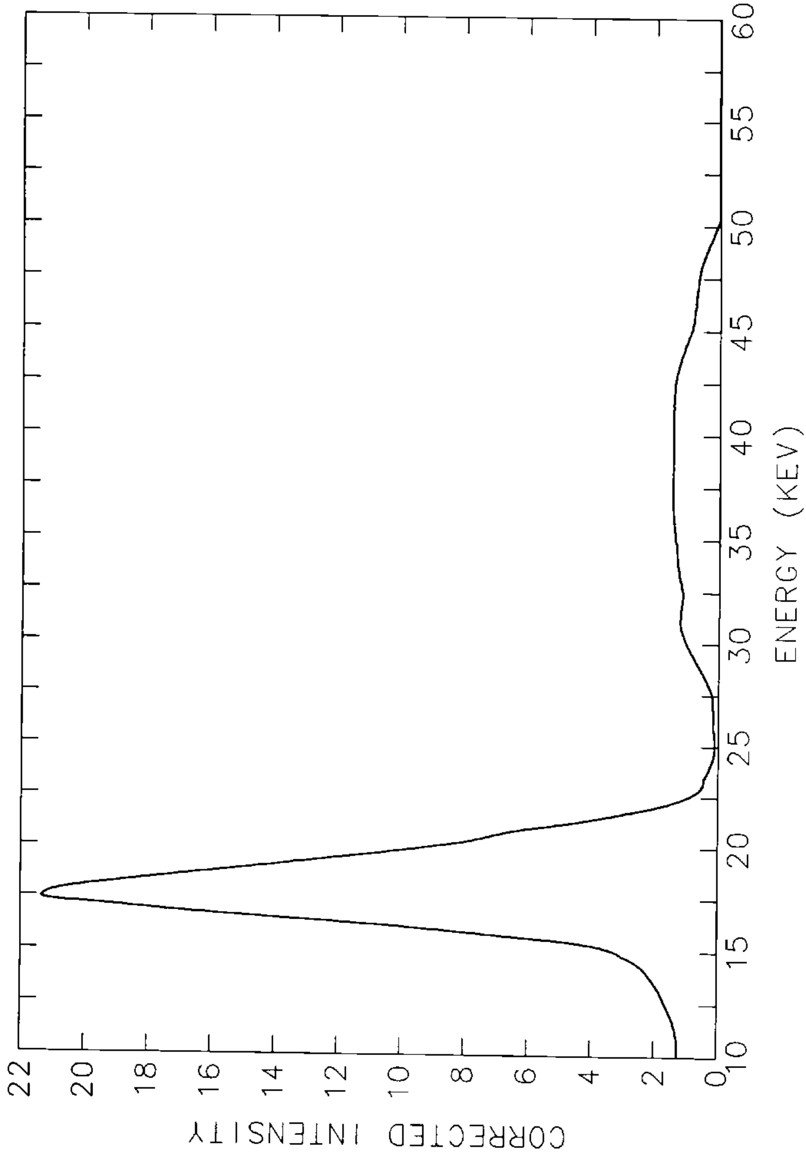

Figure 4. Measured X-ray spectrum for a 3-mil-thick Molybdenum target through a 3-mil-thick Molybdenum filter. The response of the system has been unfolded.

Table 2. Results of Linac Studies of 0.035 *M* SG-180 in PC (L-360) with Added Organometallic Compounds

Scintillator	RT (nsec)	FWHM (nsec)	DECAY (nsec)	IRT (nsec)	Peak[a]	Int.[a]
System Response (Suprasil)	0.15	0.22	0.08	0.54	—	—
100% TMGE	0.16	0.25	0.11	1.25	—	—
0.035 *M* SG-180 (100% PC)	0.55	2.56	1.80	5.26	1.00	1.00
0.035 *M* SG-180 10% TMGE	0.55	2.56	1.75	5.34	1.03	1.04
0.035 *M* SG-180 25% TMGE	0.60	2.61	1.80	5.45	0.90	0.91
0.035 *M* SG-180 35% TMGE	0.55	2.61	1.80	5.69	0.76	0.78
0.035 *M* SG-180 70% TMGE	0.55	2.71	1.80	5.49	0.65	0.68
0.035 *M* SG-180 10% TMPB	0.26	1.92	1.38	3.86	0.42	0.33
0.035 *M* SG-180 20% TMPB	0.18	1.74	1.31	3.28	—	0.22
0.035 *M* SG-180 10% TEPB	0.20	0.89	0.99	2.71	—	—
0.035 *M* SG-180 20% TEPB	0.17	0.41	0.46	1.72	—	—

[a]Peak and Int. values referenced to L-360.

age of germanium by weight, 38.5% vs 55% for the tetramethyl compound. There is also a question of long term chemical stability of solutions containing TMGE. Further studies are contemplated.

Tetramethyllead and Tetraethyllead

The lead compounds were disappointing in that they quenched the emission seriously. Addition of 10 vol% of TMPB reduced the light output to less than 50%. When 20% TMPB was added the signal was dominated by the Cerenkov contribution, precluding any conclusive information. It was hoped that the somewhat larger alkyl groups in TEPB would reduce the extent of quenching, but it appeared to be somewhat worse. In addition, there was some decomposition, possibly photochemical, of the TEPB as the solutions stood in the hood before testing. A small amount of a clear, apparently crystalline, precipitate accumulated on the bottom of the sample vials.

Table 3 shows the relative sensitivities of L-735A and L-735A-10T to 17-keV X-rays. Included in the table are predicted relative sensitivities when 10 vol%

Table 3. Effects of the Addition of 10 Volume Percent TMGE, TMSN, or TMPB or BN Containing 0.01 *M* LDS-722 and 0.10 *M* C-540A. Sensitivities are Relative to the Scintillator with no Organometallics. Excitation was by Molybdenum-filtered Molybdenum X-rays.

Fluor Candidate	Relative Energy Absorption	Predicated Relative Brightness	Observed Relative Brightness
0.01 *M* LDS-722; 0.10 *M* C-540A in:			
100% BN	1.00	1.00	1.0
10% TMGE / 90% BN	3.04	2.74	—
10% TMSN / 90% BN	3.15	2.84	2.8
10% TMPB / 90% BN	4.02	1.33[a]	—

[a]Includes quenching by the TMPB.

TMGE, TMSN, or TMPB is added to BN. Energy absorption coefficients, as tabulated in Reference 6, were used to generate curves for the BN-based scintillators. These curves were folded with the X-ray spectrum shown in Figure 4. The relative energy absorbed, the predicted brightness, and the observed brightness are shown in Table 3. The predicted relative sensitivities include a factor for the dilution of the BN, and in the case of the lead compound, consideration for the quenching by the lead compound. The agreement between the predicted and observed values for TMSN is excellent.

CONCLUSIONS

The compound TMSN still appears to be the best compound that we have tested to enhance the sensitivity of an organic scintillation solution to low energy X-rays. Although the addition of lead would greatly increase the energy deposited, the severity of the quenching more than offsets the gain made, and no further work is anticipated with these lead compounds. BBTMGE shows promise as an additive for lower energy X-rays. There may be more work in this direction once the question of long-term chemical stability is resolved.

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APPENDIX

BA	benzyl alcohol (alpha-hydroxy toluene)
BN	benzonitrile (phenyl cyanide, cyanobenzene)
BHTP (4-BHTP)	4-bromo-4″-(5-hexadecyl)-p-terphenyl
C-480	Coumarin 480 (or Coumarin 102)
C-540A	Coumarin 540A (or Coumarin 153)
DCM	red-emitting styryl laser dye, also Kodak dye No. 14567
LDS-722	far-red-emitting styryl laser dye (Exciton)
LDS-821	near-infrared-emitting styryl laser dye (Exciton)
PC	pseudocumene (1, 2, 4-trimethylbenzene)
PBD	2-phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole
Rh-610P	Rhodamine 610 perchlorate
SG-180	4,4″-di-(5-tridecyl)-p-terphenyl
SR-640	Sulforhodamine 640
TMSN	tetramethyltin
TPB	1,1,4,4-tetraphenylbutadiene