

LUMINESCENCE OF PLASTIC SCINTILLATORS

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1. INTRODUCTION

SCINTILLATION methods of counting and investigating ionizing radiations employ essentially three classes of luminescent substances: inorganic crystals, organic substances, and inert gases. Plastic scintillators, which are solid solutions of organic luminescent substances in transparent plastics (polystyrol or polyvinyl toluol)* form a special group among the organic scintillators, apart from crystals and liquid solutions. Plastic scintillators (*PS*) have a relatively high light yield, amounting to one half or two thirds of the light yield of anthracene single crystals, which is the best of all known organic scintillators in this respect. The *PS* are "fast" detectors of ionizing particles. The average scintillation lasts from 10^{-9} to 10^{-8} seconds. By a suitable choice of luminescent additives it is possible to bring the glow spectrum of *PS* into good agreement with the spectral sensitivity of the registering instruments (photoelectronic multiplier). *PS* have good mechanical strength, are not hygroscopic, can be used inside evacuated apparatus, and also over a wide range of temperatures. If, furthermore, one takes into consideration the simplicity in manufacture and the relatively low cost of *PS*, their advantages over both single crystals and liquid scintillators become evident.

Plastic scintillators have been treated in a large number of papers. Various methods of manufacture of *PS*, and the luminescent characteristics which are of importance in the practical utilization of these scintillators have all been reported. In addition, the literature contains results of investigations on the luminescence of *PS*, which are also of great theoretical interest. The distinguishing characteristics of these systems, namely the possibility of introducing various types of impurities and the almost complete absence of diffusion of molecules or radicals, allow certain important information to be obtained concerning the mechanism of glow of organic substances

*Several hypotheses have been advanced concerning the aggregate state of luminescent additives in plastics. See below.

under the influence of ionizing radiations (radio-luminescence).

In the present article we have attempted to systematize the available data on plastic scintillators. We took account of the fact that some of the results have been gathered in monographs¹⁻³ and survey articles⁴⁻⁷. Ref. 5 contains also a survey of the experimental methods of investigating scintillation properties.

2. METHODS OF PRODUCTION

The luminescent characteristics of *PS* depend substantially on the composition of the scintillator (the base substance and the luminescent additives) and on the method of production. From among the tested production methods,⁸⁻¹² the best results were obtained by polymerization of solutions of luminescent substances in certain monomers, namely: styrol,⁹⁻¹³ mixture of styrol and vinyl tetraline,¹⁴ and vinyl toluol.¹⁵ Two methods of polymerization are used: polymerization in the presence of a catalyst at low (50°C)¹⁴ or medium (120°C)^{9,16} temperatures, and thermal polymerization at medium (140°C)^{15,17} or high (200°C)^{18,19} temperatures. The first method is rarely used at present, since the catalyst reduces greatly the light yield of the *PS*.²⁰ The presence of oxygen in the polymerization process is equally undesirable. The oxygen is removed by freezing the solution⁹ or by nitrogen bubbling.^{19,21}

Thermal polymerization techniques, which make possible the preparation of large plastic scintillators, have been developed.²²⁻²⁴ Thus, for example, polystyrol-base scintillators 107 cm in diameter and weighing approximately 100 kilograms were produced.²⁴ However, a more promising method of producing plastic scintillators of large size and arbitrary form is, apparently, by die casting of ready-made luminescent plastics.^{7,21}

For certain application of scintillation methods, very thin scintillators are necessary. Thin *PS* (to 0.02 mm) have been prepared by pressing scintillating plastics at a temperature somewhat lower than the melting point.²⁵

The greatest light yield (scintillation efficiency) is possessed by a *PS* based on polyvinyl toluol with

n-terphenyl or PBD additives.* Thus, scintillators prepared by thermal polymerization of vinyl toluol (at 125° C for four days) with additives of 2% PBD and 0.1% PPS have an efficiency equal to 55% of that of an anthracene crystal.¹⁷ According to the advertised claims, the efficiency of the PS type NE-102 is 60 to 65% of commercially available anthracene. Data on other effective PS with polystyrol and polyvinyl toluol bases are found also in refs. 26--28.

3. LIMINESCENT CHARACTERISTICS

The most important characteristics of a scintillation counter are its energy and time resolution. The quantities depend both on the parameters of the photomultiplier and on the properties of the scintillator. The time resolution depends on the time distribution of the luminescence photons that are incident on the photomultiplier, i. e., on the form of the scintillation. The energy resolution of the counter is determined by the amount of energy absorbed in the scintillator per photoelectron emitted from the photomultiplier cathode, i. e., it depends on the number and spectral distribution of the photons incident on the multiplier. Still another important characteristic of a scintillation counter is the degree of its "proportionality". In a proportional counter the output pulse of the photomultiplier should be directly proportional to the energy absorbed in the scintillator. Since one can assume that the multiplier gives a linear amplification, the question of counter proportionality reduces to the question of the dependence of the luminescence yield on the energies of the various ionizing particles. Thus, the properties of a scintillation counter are directly related to such scintillator characteristics as the luminescence yield, glow spectrum, and duration of scintillation.

The luminescent characteristics depend not only on the substance of the scintillator but also on its dimensions and conditions of light gathering, since in the case of complex molecules there is a considerable overlap of the absorption and emission

spectra.²⁹ The absorption of the intrinsic luminescence, or reabsorption, is accompanied by secondary fluorescence. Reabsorption, generally speaking, results therefore in a redistribution of the photons in the external glow spectrum (attenuation of the short-wave portion of the spectrum), in a reduction of the yield, and in an increase in the duration of the glow. Therefore the external, or technical, characteristics can differ substantially from the "internal" or physical ones.

3.1. Glow Spectra

It is known that the fluorescence spectra of organic substances always correspond to transitions from the first electronic excitation levels of the molecules to the ground state (independent of the wavelength of the exciting light). Experiments show that this rule holds also for the excitation by high energy particles--the radioluminescence spectra coincide with the fluorescence spectra. In particular, this is true also for substances from which plastic scintillators are prepared.^{9, 19, 30} However, the situation is somewhat more complicated in the case of plastic scintillators. The exciting ionizing radiation is absorbed principally in the base component, since the concentration of the additives usually does not exceed several percent. The electron excitation energy is partially transferred to the molecules of the additive in a non-radiative manner, and leads partially to fluorescence of the base component (see Sec. 4.3). If the concentration of additives in the plastic scintillator is very small or if the scintillator is thin, the external glow spectrum contains this fluorescence, attenuated by absorption in the additive.³⁰

The fluorescence spectra of the additives in plastic scintillators correspond in most cases to the spectra of the same substances in liquid solutions. An exception is observed for anthracene,³¹ which enters into a chemical bond with the polystyrol,³¹⁻³³ and also for n-terphenyl in polystyrol, the fluorescence spectrum of which (at concentrations greater than 1%) contains the bands of the crystal.³⁴ Table I indicates the positions of the maxima of the molecular fluorescence spectra of certain organic compounds used for the production of plastic scintillators.

The influence of reabsorption on the glow spectra of polystyrol can be seen from Fig. 1. The ordinates represent the relative number of photons per unit wavelength interval, and the spectral curves are normalized to the long-wave section. The degree of reabsorption depends on the dimensions of the plastic scintillator and on the additive. However, even in scintillators of small

*From here on we use the following abbreviated notation for names of chemical compounds: n-terphenyl -- 3P; 2,5-diphenyl 1,3-oxazol -- PPO; 4,4'-diphenylstilbene -- PPS; 1,1',4,4'-tetraphenyl-1,3-butadiene -- 4PB; 1,3,5-triphenyl- Δ^2 -pyrazoline -- 3PP; 2-phenyl-5(4-biphenyl)-1,3,4-oxidiazol -- PBD; 2-(1-naphtyl)-5-phenyloxazol -- 6NPO; 2,5-di-[4-biphenyl]-oxazol -- BBO; quarterphenyl -- 4P; 1,5-diphenyl-3- Δ^2 -pyrazoline -- PPS₄P; 1,4-di-[2-(5-phenyloxazolyl)] -- benzol -- POPOP; 2,5-diphenyl-1,3,4-oxydiazol -- PPD.

TABLE I. Maxima of molecular spectra of fluorescence of certain organic substances,^{9, 14-17, 19, 30, 32, 35, 37}

Chemical compound	$\lambda_{\max}, m\mu$	Chemical compound	$\lambda_{\max}, m\mu$
Polystyrol	310	PPS	409
Polyvinyl toluol	~315	POPOP	420
3P	344	α NPO	402
PPD	~350	BBO	408
PBD	~370	4PB	435
PPO	382	3PP	436
4P	375-390	PPS _t P	490

volume ($\sim 1 \text{ cm}^3$), reabsorption causes the loss of a considerable fraction of the photons.³⁰ The reabsorption is substantially less in plastic scintillators with two luminescent additives. In these scintillators the excitation energy is transferred nonradiatively from the base substance to the first additive ($\sim 3\%$ by weight) and from it to the second additive ($\leq 0.1\%$) via the photon mechanism. The concentration of the second additive is sufficient

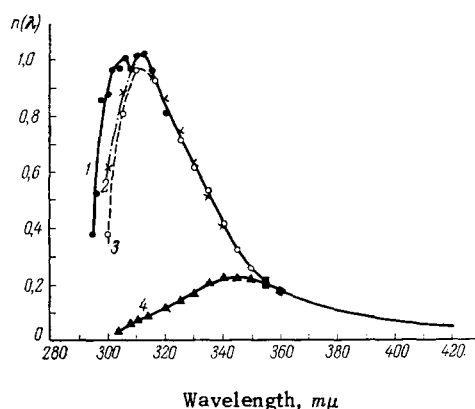
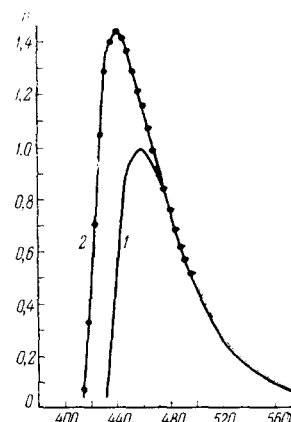


FIG. 1. Luminescence spectra of polystyrol.³⁷ 1--excitation by the Hg 2537 Å line, specimen thickness 0.5 mm, measurement on the excitation side. 3--the same, measured in direction of exciting radiation ("by transmission"). 2--excitation by β particles, measured "by transmission," thickness 0.5 mm. 4--the same, thickness 10 mm.

for almost complete absorption of the fluorescence of the first additive, but is still small and causes little self-absorption (Fig. 2). The influence of the second additive (or the spectrum mixer) is not confined to reabsorption. The spectrum mixer changes the very kinetics of the glow process (Section 3.3).

FIG. 2. Luminescence spectra of plastic scintillators with 0.017 g/g 3PP (curve 1), and with 0.02 g/g 3P and 0.0006 g/g 3PP (curve 2).³⁷ S Specimen thickness 10 mm. Excitation-- Δ particles.



3.2. Luminescence Yield. Scintillator Amplitude

The absolute energy yield of photoluminescence is defined as the ratio of the total glow energy to the absorbed exciting energy.²⁹ It is assumed here that there is no fluorescence reabsorption inside the luminophor, i. e., the energy ratio is taken for a volume element $\Delta v \rightarrow 0$.³⁸ In excitation by corpuscular radiation* the energy lost by the primary particle in a certain scintillator volume element may cause excitation of molecules located at a finite distance from this element (owing to fast secondary electrons). Therefore the fluorescence energy yield of an ionizing particle of energy E can be defined as

$$B = \frac{dL}{dE}, \quad (1)$$

where dE is the energy lost by the particle along a path dx , and dL is the energy of the luminescence light, excited because of dE . **

Experience has shown that the yield of organic substances in the condensed phase depends, generally speaking, on the velocity and charge of the particle. As the specific loss dE/dx is decreased, the yield increases, reaching a maximum value B_0 at $dE/dx \cong 4 \text{ Mev/cm}$.⁴⁰ On the basis of (1), the mean yield from a completely stopped particle of initial energy E_0 will be

$$\bar{B} = \frac{1}{E_0} \int_0^{E_0} B(E) dE = \frac{L}{E_0}, \quad (2)$$

where L is the summary luminescence energy. If the mean photon energy in the emission spectrum is $h\bar{\nu}$, then the amplitude of the scintillation (number of photons per flash) is

$$S = \frac{E_0}{h\bar{\nu}} B_0, \quad (3)$$

*For γ or x rays the excitation is due to secondary electrons, for neutrons it is due to recoil nuclei or products of nuclear reaction.

**We mean only energy losses due to excitation and ionization of the scintillator substance.

and the specific amplitude of the scintillation (or the number of photons per unit of absorbed excitation energy) is

$$s(E) = \frac{B(E)}{h\nu} \text{ and } \bar{s} = \frac{\bar{B}}{h\nu}. \quad (4)$$

Scintillators are used not only for particle counting, but also for measurement of radiation intensity or for dosimetry. In this case it becomes meaningful to speak of the energy yield of luminescence for a given radiation, i. e., of the quantity

$$\bar{B} = \frac{\Phi}{D}, \quad (5)$$

where Φ is the luminescence intensity, D the dose absorbed in the scintillator. The quantity \bar{B} depends on the spectrum of the primary exciting particles, $\sigma(E_0)$:

$$\bar{B} = \frac{\int B(E_0) E_0 \sigma(E_0) dE_0}{\int E_0 \sigma(E_0) dE_0}.$$

Measurement of the energy yield of radio-luminescence involves three problems:⁴¹ 1) determination of the absolute sensitivity of the photomultiplier in the wavelength interval of interest, 2) determination of the exciting radiation energy absorbed by the scintillator, 3) determination of the total luminescence energy from the measured light flux incident on the photomultiplier. The greatest difficulties are caused by the last problem, particularly in connection with the need for accounting for self-absorption and secondary fluorescence. Certain methodological indications are contained in refs. 41--44. A detailed description of the procedure as applied to plastic scintillators excited by γ rays is given in ref. 39. For plastic scintillators with 1.5×10^{-2} g/g $4PB$ added, prepared by thermal polymerization at high temperature,¹⁹ the energy yield is

$$\bar{B} = 0.038$$

(excitation by γ rays from Co^{60}). Since the mean photon energy in the spectrum of $4PB$ is 2.66 eV, the specific scintillation amplitude is

$$\bar{s} = 0.014 \text{ photons / eV}.$$

The corresponding value for crystalline anthracene ranges from 0.021 (ref. 43) to 0.036 (ref. 42), i. e., is approximately twice as large.

*In γ excitation this is the spectrum of the Compton electrons and photoelectrons.

In other papers reporting on the determination of the luminescence yield of plastic scintillators, the external yields of plastic scintillators were compared with the yield of crystalline anthracene or stilbene without allowance for the differences in the glow spectra and degree of reabsorption, i. e., the so-called scintillator efficiency relative to anthracene or stilbene was given. This efficiency depends on the dimensions of the scintillators and on the spectral sensitivity of the photomultiplier^{3, 28} (see also Table II). In addition, the scintillation

TABLE II. Relative efficiency of plastic scintillators of various sizes as a function of the luminescent additives and of the photomultiplier.⁴⁵ The plastic scintillator had a polystyrol base.¹⁹ The specimens were cylindrical. Excitation with β particles from Ce^{144} -- Pr^{144}

Additives	Concentration in gram per 100 gram of styrol	Relative efficiency with:					
		FEU-19			FEU-1C		
		at a specimen height, mm					
		10	20	30	75	20	30
$3P+3PP$	$2+0.04$	50	50	50	50	50	50
$3P+4PB$	$3+0.02$	50	48	47	—	49	46
$3P+4P$	$3+0.1$	56	49	45	33	38	34
PPO	1.3	54	46	43	24	37	34
$PPSiP$	1.8	20	—	17	—	—	23

characteristics of stilbene crystals and particularly of anthracene crystals depend strongly on the manufacturing methods and on the storage conditions.⁵ All this makes it difficult, sometimes even impossible, to compare the results obtained by various authors. Table III lists the relative efficiencies of several types of plastic scintillators made by the British firm Nuclear Enterprises and of our own plastic-scintillator specimen⁴⁵ used with various photomultipliers, and also the "technical" scintillation amplitude, which characterizes these plastic scintillators without reference to the photomultiplier.

Let us now consider the investigations of the "proportionality" of plastic scintillators. Dhar⁴⁶ measured the photomultiplier output pulse amplitude (H) produced in response to excitation of a plastic scintillator ($3P+4PB$ in polyvinyl toluol) by monoenergetic electrons ($E = 290 - 980$ keV). H increased faster than E , at least up to 800 keV. In contrast with this, Bisi et al.⁴⁷ found H to be proportional to E in the electron energy range from 180 to 2380 keV.⁴⁸ A linear relation between H and E was also obtained⁴⁸ for plastic scintillators with $4PB$ (electron energy 478--1040 keV). The luminescence yield decreases with energy for α par-

TABLE III. Relative efficiency of plastic scintillators with different photomultipliers.⁴⁵ Cylindrical specimens measuring 1.1 inch and 1 inch high without reflectors.

Scintillator	Relative efficiency* with:			External magnitude of scintillations**
	FEU - 29	FEU - 1C	RCA-5819	
Pamilon	52	56	54	62
NE-101	54	58	56	62
NE-102	60	60	60	60
PS -1***)	48	52	49	53
PS -2	61	67	63	65
PS -3	56	53	53	53

*Measurements based on the average current at excitation with β particles from Ce^{144} -- Pr^{144} and based on the heights of the pulses for 624-keV electrons give equivalent results. For NE-102, the efficiency is taken to be 60.
 **Measurement with the aid of a quantum counter, which makes optical contact with the scintillator. Arbitrary units.
 ***PS-1: 3P+3PP in polystyrol; PS-2: the same in polyvinyl toluol; PS-3: 3P+PPS in polyvinyl toluol.

ticles. The decrease is faster than in crystal line anthracene.⁴⁸

The "nonlinearity" of a scintillator is customarily characterized by the so called α/β ratio, the ratio of the two average luminescence yields of particles from Po^{210} and high-energy electrons, i. e.,

$$D_{\alpha\beta} = \frac{\bar{B}_\alpha}{\bar{B}_\beta} = \frac{H_\alpha E_\beta}{E_\alpha H_\beta}.$$

For organic crystals, the α/β ratio is approximately 0.10^{4, 5, 49} For liquid and plastic scintillators it ranges from 0.08 to 0.12.^{5, 49-51} Here $D_{\alpha\beta}$ depends on the concentration of the luminescent substance. Thus, for n-terphenyl in toluol $D_{\alpha\beta} = 0.06$ at a concentration of 0.2 g/l and 0.09 at a concentration of 8 g/l. The data of reference 35 yield for plastic scintillators an inverse concentration dependence: $D_{\alpha\beta}$ decreases with increasing concentration of the additive.

The luminescence yield of plastic scintillators depends on the temperature. References 18, 53, and 54 are devoted to an investigation of this dependence. It was found, in particular, that for certain types of plastic scintillators the external radioluminescence yield changes little over a wide range of temperatures. For other plastic scintillators, the temperature dependence is stronger and is sometimes characterized by a sign reversal (Table IV). The temperature quenching depends on the concentration of the additives and diminishes with increasing concentration (Fig. 3). A comparison with the temperature quenching of the fluorescence of the additives shows that the con-

centration effect is connected with an increase in the efficiency of the non-radiative excitation-energy transfer from the polystyrol to the additive.^{53, 54}

TABLE IV. Plastic scintillator efficiency as a function of the temperature.⁵⁴ Scintillators with polystyrol base.¹⁹ Cylindrical specimens 16 mm in diameter and 10 mm high. Excitation with γ rays from Co^{60} . Measurement of intensity of glow of FEU-19. The temperature of the FEU was not measured.

Luminescent additive	Concentration, gram per 100 gram	Relative efficiency at the following temperature (°K):					
		100	140	190	240	290	340
Pure polystyrol	—	52	41	32	24	17	11
4PB	1,5	98	106	110	108	100	78
3PP	1,0	104	103	102	101	100	92
3P+4PB	3,0+0,05	134	134	133	132	122	108

For pure polystyrol, the temperature radioluminescence quenching (excitation with α , β , and γ rays) does not differ from fluorescence quenching, within a measurement accuracy range of $\pm 5\%$.⁵³

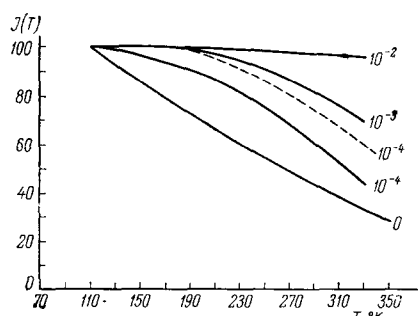


FIG. 3. External yield of luminescence of a plastic scintillator with 3PP as a function of the temperature.⁵⁴ Excitation with γ rays. Specimen thickness 10 mm. The numbers against the curves indicate the concentration of the additive (in g/g). The curves are made coincident at $T = 110^\circ K$. Dotted curve--excitation with α particles.

An important characteristic of the scintillator is its radiation stability. It is known, for example, that the amplitude of anthracene scintillations is reduced by one-half after exposure to a flux of approximately 10^{11} α particles from Po^{210} per cm^2 , or to approximately 10^{14} 4-kev electrons per cm^2 (reference 1). The radiation stability of scintillators with a polystyrol base is considerably higher^{33, 55} (see Table V). In this case the yield

TABLE V. Damage to polystyrol-base scintillators irradiated by α particles from Po^{210} (references 55 and 56)

Luminescent additive	Concentration, g/100-g	Dose (erg/g) causing a reduction to 1/2	
		Transmission of light of its own luminescence	luminescence yield
Pure polystyrol	—	$1.6 \cdot 10^{10}$	—
4PB	1.5	$32 \cdot 10^{10}$	$9.0 \cdot 10^9$
3P+4PB	2.5 ± 0.01 to 0.12	—	$6.1 \cdot 10^9$
Anthracene crystal	—	—	$5.6 \cdot 10^9$ $1.0 \cdot 10^8$ ⁵⁷

of the radiation-damage reaction produced by β rays is approximately 1/6 to 1/8 that produced by α particles.⁵⁶ Irradiation of pure polystyrol, and also of scintillators in which it serves as a base, is accompanied in the presence of air by reduction in emission of intrinsic luminescence and a faster decrease in yield (Table V). The coefficient of additional absorption increases in proportion to the radiation dose received by the scintillator. Thus, in irradiation with α particles the coefficient of

absorption for the group of mercury lines ($\lambda = 366 m\mu$) is

$$\mu = 3.4 \cdot 10^{-9} D \text{ cm}^{-1},$$

where D is the dose in erg/gram. This relation has been verified up to $D \approx 6 \times 10^{11}$ erg/g.⁵⁶

The authors of references 55 and 56 offer the following explanation for the kinetics of radiation damage of scintillators with a polystyrol base. The ionizing radiation produces in the polystyrol chemical substances which are highly absorbing in the ultraviolet region of the spectrum (see also references 58 and 59). The reaction has a relatively low yield, and this insures proportionality between the concentration of the radiation-damage product and the dose, up to very high doses. The radiation-damage products cause dynamic quenching of the luminescence of the polystyrol and principally static quenching of the additives (or quenching of second and first order respectively). The dynamic character of the quenching of the glow of polystyrol is confirmed by the reduced duration of glow with increasing dose.⁴⁵

3.3 Duration of Glow. Form of Scintillations

The kinetics of scintillations in plastic scintillators is determined by the presence of additional quenching, due to the specific nature of the excitation by ionizing particles, by the excitation-energy transfer to the luminescence additive, and by the fluorescence of the additive. An investigation of the kinetics of the glow is an important means of clarifying the mechanism of these processes and, in particular, of the transfer of excitation energy.⁶⁰ We begin the examination with the final stage of the scintillation -- fluorescence of the additive.

The fluorescence of dilute solutions of organic substances attenuates exponentially. This can be readily understood. All the excited molecules are under identical conditions, and there are no interactions between them. In concentrated solutions or in the presence of inductive-resonance excitation-energy transfer to any other substance, the attenuation is no longer exponential.^{61, 62} Generally speaking, the exponential nature of the attenuation of fluorescence may also be violated because of reabsorption with the accompanying secondary fluorescence.^{63, 64}

At the present time the most sensitive method of determining whether the attenuation of short-duration glow is exponential is the fluorometric method. It is well known that the difference in

phase ϕ between the intensity of the glow and the exciting radiation, modulated at a frequency ω , is related to the attenuation $L(t)$ by the following formula

$$\tan \varphi = \frac{\int_0^{\infty} L(t) \sin \omega t dt}{\int_0^{\infty} L(t) \cos \omega t dt} \quad (6)$$

In the case of an exponential law

$$L(t) = L_0 e^{-\lambda t}$$

the "fluorometric time"

$$\tau^f \equiv \frac{1}{\omega} \tan \varphi = \frac{1}{\lambda} = \tau$$

is independent of the modulation frequency and equals the mean duration of glow. Thus, to test whether the attenuation is exponential it is enough to measure ϕ for several values of ω . Such measurements were carried out for plastic scintillators in a multiple-frequency fluorometer with electron beam.⁶⁵ It was found that, within the limits of accuracy of measurements ($\pm 2 \times 10^{-10}$ sec), the fluorescence of 4PB and 3PP in polystyrol attenuates exponentially, in spite of the considerable increase in the mean duration with concentration of the additive (Fig. 4). These results are in agreement with the theory.⁶⁴

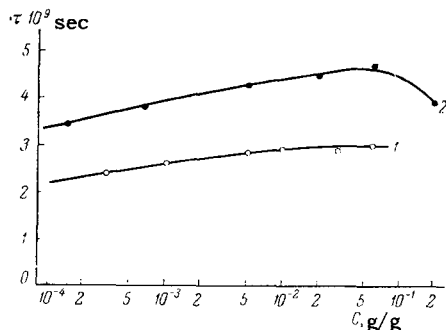


FIG. 4. Mean fluorescence time of additives in a plastic scintillator as a function of the concentration.⁶⁴ Curve 1--4PB, 2--3PP.

The kinetics of scintillations of plastic scintillators with one luminescent additive is considered in reference 66. If N_{10} molecules of the main substance and N_{20} molecules of the additive are excited at $t = 0$, then

$$\frac{dN_2}{dt} = -\lambda_2 N_2 + N_{10} R_1(t) \quad (7)$$

or

$$N_2(t) = N_{10} e^{-\lambda_2 t} \left\{ \alpha_2 + \int_0^t R_1(t') e^{\lambda_2 t'} dt' \right\}, \quad (8)$$

where $\lambda_2^{-1} = t_2$ is the fluorescence time of the

additive, with allowance for secondary glow, $N_{10} R_1(t)$ is the number of excitation-energy transfers from the main substance to the additive per unit time at the instant t , and $\alpha_2 = N_{20}/N_{10}$. By definition, the mean scintillation time is

$$\tau_s = \frac{\int_0^{\infty} t dN_2}{\int_0^{\infty} dN_2},$$

where dN_2 is the number of molecules of the additive that lose their excitation energy within the time interval $(t, t+dt)$. Calculations yield

$$\tau_s = \tau_2 + \tau_{12}, \quad \tau_{12} = \frac{\int_0^{\infty} t R_1(t) dt}{\alpha_2 + \int_0^{\infty} R_1(t) dt} \quad (9)$$

The mean scintillation time τ_s , exceeds the fluorescence time of the additive τ_2 by a quantity τ_{12} , which depends on the mechanism of the excitation-energy transfer from the main component to the additive.

An experimental determination of τ_{12} was made with a multiple-frequency phase fluorometer.⁶⁵ Subject to an attenuation law (8), formula (6) yields

$$\varphi_s = \varphi_2 + \varphi_{12}, \quad (10)$$

$$\tan \varphi_2 = \omega \tau_2, \quad \tan \varphi_{12} = \frac{\int_0^{\infty} R_1 \sin \omega t dt}{\alpha_2 + \int_0^{\infty} R_1 \cos \omega t dt}.$$

Consequently, by measuring ϕ_s and ϕ_2 separately it is possible to calculate the "fluorometric time" of transfer

$$\tau_{12}^f = \frac{1}{\omega} \tan \phi_{12}$$

The results of the measurements for 3PP in polystyrol are shown in Fig. 5. The rapid reduction in

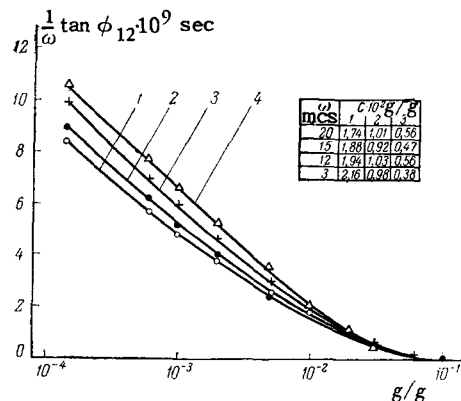


FIG. 5. "Fluorometric time" of transfer as a function of the concentration of 3PP in a plastic scintillator.⁶⁶ Modulation frequency: Curve 1--20 Mcs, 2--15 Mcs, 3--12 Mcs, 4--8 Mcs.

TABLE VI. Time of additive fluorescence, t_2 , and scintillation time, t_s , in plastic scintillators.

Composition of scintillator	τ_2 10^{-9} sec	τ_s 10^{-9} sec
Pure polystyrol		16 ³⁵
Polystyrol + 0.015 g/g 3PP	4.6 ⁶⁶	6.0 ⁶⁶
Polystyrol + 0.015 g/g 4PB	2.9 ⁶⁶ 2.8 ¹⁶	6.5 ³⁵ 4.6 ⁵ 5.0 ⁶⁹ 4.3 ⁶⁶ 4.0 ⁵ 4.4 ⁶⁹
Polystyrol + 0.03 g/g 3P + 0.0002 g/g 4PB		< 3.0 ⁵
Polystyrol + 0.04 g/g 3P	2.7 ¹⁶ 1.7 ²⁷	3.5 ⁶⁹
Polystyrol + 0.03 g/g 3P + 0.001 g/g 4P .	3.3 ²⁷ for 4P	4.2 ⁶⁹
Polystyrol + 0.013 g/g PPO		< 3.0 ⁷⁰
Polyvinyl toluol + 0.04 g/g 3P		4.0 ⁷⁰
Polyvinyl toluol + 0.04 g/g 3P + 0.0002 g/g 4PB		< 3.0 ⁷⁰
Polyvinyl toluol + 0.04 g/g 3P + 0.001 g/g PPS		< 3.0 ⁷⁰

Methods of scintillation measurements: references 5, 35, and 70 -- oscillography of an RCA-5819 photomultiplier current excited by x-ray pulses; reference 66 -- oscillography of the current of a FEU-IV photomultiplier excited by a Po-Be compound; reference 69 -- phase method with excitation by 30-keV electrons.

with increasing concentration of 3PP is evidence that at high additive concentrations the excitation-energy transfer is principally nonradiative, i. e., it occurs before the photons are emitted by the polystyrol. At a higher transfer speed, R_1 reaches negligibly small values even at $t \ll 1/\omega$, and its value, according to (10) and (9), should be

$$\tau_{12}^{\text{fl}} \cong \tau_{12}$$

According to Fig. 5 this takes place for an additive concentration $c \approx 0.01$ g/g, when

$$\tau_{12} \leq 1.5 \cdot 10^{-9} \text{ sec.}$$

Attention must be called, however, to the following circumstance. It is known that the "technical" scintillation time in organic crystals exceeds the fluorescence time.¹ At the same time, Eq. (7) contains the suggestion that the glow time of the additive is the same when excited by particles as in photoexcitation. Experiment confirms the correctness of this assumption, particularly for electrons: at high concentrations of the luminescent substance the scintillation time t_s coincides with the fluorescence time.^{66, 67}

Thus, in a plastic scintillator with optimum concentration of additive (Section 2), the form of the scintillation is characterized by the presence of a maximum at $t \sim 10^{-9}$ sec. After the maximum is reached, the attenuation of scintillation should follow an exponential law with a time constant $\cong t_2$ (reference 66). Unfortunately, the large time dispersion of the photomultipliers ($> 10^{-9}$ sec.) does not make it possible as yet to investigate the initial portion of the scintillation curve by means of direct oscillograms.⁶⁸ Usually the initial section of the oscillograms is discarded and the mean scintillation time is determined from the

decreasing portion. The data available in the literature have been gathered in Table VI. Only in the case of plastic scintillators with 4PB do we have results obtained by different methods. The lack of agreement between the "oscillographic"^{35, 69} and "fluorometric"⁶⁶ data is possibly due to insufficient allowance for the time dispersion of the photomultiplier in the oscillographic measurements.

The presence of a second additive or spectrum mixer ($c < 10^{-3}$ g/g) in the plastic scintillator complicates the kinetics of the glow, since an additional process appears -- the transfer of energy from the first additive to the spectrum mixer, proceeding principally via the photon mechanism. Thus, it follows from Table VI that the addition of 4PB or 4P to scintillators with n-terphenyl leads to an increase in the scintillation time. It is somewhat less than the fluorescence time of the spectrum mixer (Table VII), owing to the absence of secondary fluorescence of the first additive and the presence of non-radiative transfer to the mixer.

TABLE VII. Increase in the mean duration of scintillations of plastic scintillators with 0.02 g/g 3P in polystyrol, as a function of the concentration of the spectrum mixer -3PP.⁴⁵ Excitation with electrons. Measurement by fluorometric method.⁶⁵

Concentration 3PP, g/g	$\Delta\tau_s$ (10^{-9} sec)	Fluorescence time of 3PP (10^{-9} sec)
$3 \cdot 10^{-4}$	2.9	3.6
$2 \cdot 10^{-3}$	2.8	4.1

The glow of plastic scintillators, like the glow of organic crystals, contains "slow" components. Thus, according to data of reference 71, when x-rays are used to excite a plastic scintillator based on polystyrol and polyvinyl toluol with 3P as an additive and with a spectrum mixer, three slow components are observed:

Attenuation constant (10^{-6} sec) . . .	0.13	2.5	~ 40
Yield relative to the "fast" component (%)	6	4	0.7

At low temperatures ($< 150^\circ K$) the glow of the plastic scintillator contains components which take minutes to attenuate.^{18, 54} The rate of attenuation is independent of the luminescent additive and decreases with decreasing temperature. In addition, in excitation with γ rays the plastic scintillators exhibit a temperature glow with a maximum near $120^\circ K$. Upon excitation with α particles the yield of this glow is reduced by a factor of several hundred. The author^{18, 54} relates these phenomena with radical-recombination processes, observed in polystyrol under the influence of ionizing radiation. The substantial differences between α and γ excitation are attributed here to local temperature rises in the track of the α particle.

4. ON THE SCINTILLATION MECHANISM

In an investigation of luminescence of organic substances under the influence of hard radiation (radioluminescence) it is advantageous to distinguish between two phases of the phenomenon. The first phase, deceleration of the charged particle, is accompanied by ionization and excitation of the molecules of the medium. The second phase includes all the processes that occur in the irradiated portion of the substance until the activated molecules lose their charges and excitation energy. Such a distinction is permissible, strictly speaking, only for small sections of the track, since the duration of the total retardation of the particle may be found to be comparable or even considerably longer than the duration of certain processes of the second phase. But this is quite adequate if it is considered that the direct interaction between the activated molecules is significant only at short distances ($< 100 A$).^{*} A feature of the first

^{*}It is easy to see that the "two-phase" analysis is applicable also to organic crystals, where the exciton mean free path is greater.

phase, which substantially distinguishes radioluminescence from photoluminescence, is the non-selectivity of action of the exciting radiation. This nonselectivity is twofold. Firstly, the fast charged particle is capable in final analysis of raising the molecule to any excited state or to ionize it. Secondly, the relative probability of different transitions depends little on the property of the particle itself.^{**} The second substantial feature is that the primary activations, caused by the exciting particle, are correlated in time and in space. Since in this case the spatial density of activation depends substantially on the velocity and charge of the particle, the kinetics of the second phase should also depend on these quantities.

Thus, the specific amplitude of the scintillation, or the energy yield of the radioluminescence, depends on the amount of energy spent in the excitation of one molecule, and on the ratio of the speeds of the emission and quenching processes. In multi-component scintillators the yield depends also on the efficiency of excitation-energy transfer to the fluorescent substance.

We consider below several of these questions.

4.1 Excitation and Ionization

The total number of excitation and ionization acts (electron levels) is made up of processes due directly to the primary charged particle and to secondary electrons emitted from the molecules (or atoms) during the ionization process. The kinetic energy of the secondary electrons can reach a maximum value

$$T_m \cong \frac{4m}{M} E$$

for heavy particles ($M \gg m$) and $\frac{1}{2} E$ for electrons.^{*} Fast secondary electrons (δ -electrons), in turn, excite and ionize the molecules of the medium, and this leads to the appearance of a second generation of secondary electrons, etc. Ionization by secondary electrons constitutes a considerable fraction of total ionization. Thus, for electrons with energies from 4 to 1500 keV the ratio of the specific primary ionization to the specific complete ionization is independent of the energy and equals 0.44 for hydrogen and 0.29 for nitrogen, oxygen, and argon. For hydrogen-containing compounds it has an intermediate value.⁷²

^{**}We speak here of primary elementary processes. The yields of many radiation reactions depend on the energy and charge of the particles. See, for example, Sec. 3.2

^{*}Since we cannot distinguish between the incident electron and an electron emitted from the atom, the slower one is customarily called the secondary.

TABLE VIII. Mean energy lost by charged particles in the production of a single pair of ions in certain gases (ev).

Gas	α particles		Electrons			X-rays, 2 Mev	Energy spent in one primary ionization ⁹⁴
	Po ²¹⁰	Pu ²³⁹	Al ²⁷ +H ³	H ³ , Ni ⁶³ , C ¹⁴	S ³⁵		
1	2	3	4	5	6	7	8
He	42.7	46.0	32.5	42.3		40.4	
Ne	36.8			36.6		35.3	
Ar	26.4	26.4	27.0	26.4		25.8	93
Kr	24.1			24.1		24.8	
Xe	21.9			22.0		22.1	
H ₂	36.3	37.0	38.0	36.3		36.3	80
Air	35.5	35.0	35.0	34.1	34.1	33.9	
N ₂	36.6	36.3	35.8	34.7	35.3	34.6	118
O	32.5	32.2	32.2	30.9		31.2	116
CO ₂	34.5	34.3		33.0		32.6	106
C ₂ H ₄	28.0	28.0		26.3	26.2	26.5	72
C ₂ H ₆	26.6			24.8	24.7		
CH ₄	29.2	29.4	30.2	27.3		26.8	
C ₂ H ₂	27.5			26.1			76

The table is taken from the survey by J. Weiss and W. Bernstein, Rad. Research 6, 603 (1957).
Column 6 taken from the article by W. P. Jesse and J. Sadauskis, Phys. Rev. 107, 766 (1957).

The problem of quantitatively describing the interaction between the particle and matter, which is complicated in itself, becomes still more complicated in connection with the need for accounting for a large number of secondary electrons. However, it is precisely because the secondary electrons are responsible for more than half of the ionization and excitation acts that the relative probability of these processes depends little on the energy and kind of slowing-down particle. This is clearly seen from the example of the mean energy W , lost by an ionizing particle to the production of a single pair of ions (Table VIII). For all the tremendous difference in the specific energy loss for α particles and fast electrons, there are either no differences in W at all (inert gases, hydrogen) or else they are insignificant.

Let us turn now to the question of the number of ionizations N_i and number of excitations N_e due to an energy E transferred by the particle to the moderating substance.³⁷ From the very definition of W we have

$$E = N_i W.$$

On the other hand

$$E = N_i(I_i + w) + N_e I_e,$$

where I_i is the potential of molecule ionization (with allowance for the possible ion excitation energy); w -- mean kinetic energy of slow secondary electrons, incapable of further excitation of electron levels ("non-exciting electrons"); I_e is the

average excitation energy of the molecule.* From these two relations we obtain

$$\frac{N_e}{N_i} = \frac{W - I_i - w}{I_e}. \quad (11)$$

For the luminescent substances of interest to us**

$$\frac{N_e}{N_i} \sim 3,$$

i. e., there are approximately three excited molecules for each ionized one. The total number of activations (ionization, excitation) $N_0 = N_i + N_e$, and the average energy consumed per activation is $\epsilon_0 = E/N_0 \approx 8$ ev.

We must stop to discuss two other questions. The first pertains to the activation of the impurity molecules. If the lower excitation potential of the impurity I_1 is less than the lower excitation potential of the main component I_0 , then a certain selectivity will be observed in the action of the ionizing radiation.^{73, 74} In fact, if N_0 ions (reduced to singly-charged ones) are produced by the slowing down of the particle in the first component, then they are accompanied by N_0 free "nonexciting" electrons with energies $\epsilon < I_0$. The "nonexciting" electrons with $\epsilon > I_1$ are capable of further activating the impurity molecules. This will actually

* I_i and I_e must be taken to mean quantities that are suitably averaged for each kind of molecule.

** W is measured for gases. The proportionality of ionization in gas and condensed media has not been proved, but such an assumption does not contradict experiment. We shall not stop to analyze this question, owing to lack of space.

take place if the probability of the competing process (slowing down of the electrons, production of negative ions) is sufficiently small. For example,⁷⁴ for certain gases these processes become insignificant compared with the activation of the impurity when the latter has a molecular concentration $> 10^{-3}$. The need for accounting for the role of "nonexciting" electrons in the phenomenon of radioluminescence was demonstrated in an examination of the energy transfer in plastic scintillators.⁵³

The second question concerns the lifetime of the positive ions, or the speed of recombination. Since the mean free path of slow electrons is very small when the substance has a high density, then in a condensed substance the majority of secondary electrons do not leave the field of attraction of the ions, and recombination takes place within a very short time interval. Thus, for example, the following computed values were obtained⁷⁵ for water: the slowing-down time of electrons with initial energies 15 eV amounts to approximately 3×10^{-14} sec; the time of return to the positive ion from a distance of 100 Å does not exceed 1.2×10^{-11} sec, and from a distance of 20 Å it does not exceed 2.2×10^{-13} sec.

Thus, the majority of ions in a condensed medium recombine within $\sim 10^{-12}$ sec, which essentially eliminates the difference between ionized and excited molecules: at the start of the second phase of scintillation, molecules exist with different excitation energies. However, cases are possible when the recombination time should still influence the kinetics of the glow. In fact, owing to the presence of fast secondary electrons, a certain small fraction of the ions will have long lifetimes. Their recombination is a source of excited molecules at later stages of glow, i. e., leads to an increase of the mean duration of scintillation. The influence of the effect should increase the more complete and the faster the quenching of the primary activations.*

4.2 Absolute Luminescence Yield

The maximum possible specific magnitude of scintillations is determined from the condition that all the activations are accompanied by a transfer of molecules into the "fluorescent state," i. e.,

$$s_{\max} = \frac{\eta}{\epsilon_0} = \frac{1}{8} \eta \text{ photons/cv,}$$

where η is the quantum yield of fluorescence. Experiments have yielded values that are several

times smaller. For electrons ($E \sim 1$ Mev) in anthracene, $s/n \cong 0.03$ (see Sec. 3.2). Other organic crystals,^{76,77} and also polystyrol,³⁹ have approximately the same s/n . Thus, even when excited by high-energy electrons, approximately 80% of the total number of activations are lost in organic scintillators, in addition to the photo-excitation. Several suggestions have been made considering the nature of these losses.

Galanin and Grishin⁴⁴ have calculated the absolute luminescence yield of anthracene for fast electrons under the assumption that emission of light can be produced only by direct excitation of the π -electron system of the molecule. Their result yields $s/\eta \approx 0.006$. It is quite likely that more accurate calculation can improve this number.

Birks^{1,78} believes that the first stage in the scintillation process is the recombination of the positive ions with the electrons, and that this stage leads to the emission of short-wave "primary photons." This is followed by a fast ($\sim 10^{-11}$ sec) photon cascade (alternate absorption and emission), as a result of which the "primary photons" lose a portion of their energy, but their number remains the same. Finally, ordinary fluorescence occurs. Consequently, $s = \eta/W \cong 0.03\eta$, in agreement with experiment. However, this "agreement" commands a high price. First, no account is taken of the considerably larger number of excited molecules ($N_e \cong 3N_i$). Second, the emission of "primary photons" cannot be considered experimentally proved.^{79,80} The inconsistency in Birks' theory, particularly with respect to plastic scintillators, is demonstrated by the experimental results on temperature quenching⁵³ and kinetics of radiation damage,⁵⁶ as well as on excitation-energy transfer (see Sec. 5).

According to the hypothesis by Kallman et al.⁸¹ a substantial role is played in the scintillation process by the interaction of the activated molecules with one another. Reynolds,⁵² Black,⁵⁷ and Wright^{82,83} consider that bimolecular processes of quenching cause the low scintillation yield for a particle with large specific energy loss. For electrons, the bimolecular hypothesis was developed by Rozman and Kilin.⁸⁴

The foregoing hypotheses lead to definite conclusions concerning the kinetics of scintillations. Thus, it follows from Galanin's hypothesis⁴⁴ that the scintillation time should coincide with the fluorescence time (accurate to possible differences in secondary fluorescence). According to Birks' hypothesis,¹ the kinetics of radioluminescence differ substantially from the kinetics of fluorescence: the form of the scintillations, considered as

*See also F.D. Brook, Nucl. Instr. Meth. **4**, 151 (1959).

TABLE IX. $\tau\beta^l$ of polystyrol excited by 30-keV electrons.⁸⁴

Modulation frequency ω (10^8 sec^{-1}) . . .	0.502	0.754	0.952	1.26
Phase angle ϕ	30.0	38.8	41.2	48.6
$\tau\beta^l = \frac{1}{\omega} \tan \phi$ (10^{-9} sec)	11.5 ± 0.4	10.7 ± 0.4	9.2 ± 0.3	8.9 ± 0.3
$\tau\beta^l$ theoretical (10^{-9} sec)*	11.5	10.7	9.4	8.8

*Calculated from Eq. (12) with the following values of the parameters: $\alpha_c = 0.84$, $\lambda = 6.3 \times 10^7$ (reference 35), and $\beta/\lambda = 50$.

sequences of two exponential decays, is characterized by an increase in intensity in the initial portion. Finally, in the presence of quenching due to the interaction between the activated molecules, the form of the scintillation should be characterized by the presence of a very sharp drop during the start of the process.

Attempts at an experimental determination of the form of anthracene scintillations gave contradictory results. Wright⁸⁵ determined the scintillation form by investigating the dependence of the power dissipated in the load resistance of the photomultiplier on the size of this resistance. He reached a conclusion that at the beginning of the scintillation there is a sharp decrease in glow intensity, which then slows down to exponential. At equal total scintillation amplitude, the initial peak is greater when the excitation is produced by fast electrons, and the exponential portion attenuates more slowly when the excitation is by α particles (compare with Sec. 4.1). Glaser⁸⁶ investigated the form of scintillations in excitation by cathode rays with the aid of a two-disk electron phosphoroscope. The curve he obtained, with a maximum at $t \cong 2 \times 10^{-8} \text{ sec}$, agrees with Birks' ideas,¹ although many other experimental data obtained by Glaser contradict the "primary photon" hypothesis.

Kilin and Rozman,⁸⁴ using a multiple-frequency fluorometer, measured the "fluorometric time" $\tau\beta^l$ of polystyrol at different modulation frequencies ω . It has been found (Table IX) that $\tau\beta^l$ depends on ω , i. e., the emission law is not exponential. The decrease in $\tau\beta^l$ with increasing ω contradicts the theory of "primary photons" (which leads to an inverse relation) and corresponds to the assumed

presence of bimolecular quenching. *For quantitative estimates, the authors⁸⁴ have used the following simplified scheme: At the initial instant of time the track of the fast electron consists of a certain number αN_0 of activated molecules, which are isolated from the other activated molecules, and of $\alpha_c N_0$ activated molecules located in the "conglomerations."⁸⁷ It is assumed that all the conglomerations are identical. Changes in the number of molecules in the first and second groups [$n(t)$ and $n_c(t)$ respectively] is determined by the following equations (in the absence of migration of the excitations energy)

$$\frac{dn}{dt} = -\lambda n, \quad \frac{dn_c}{dt} = -\lambda n_c - \frac{\beta}{\alpha_c N_0} n_c^2,$$

where $t = \lambda^{-1}$ is the lifetime of the excited state of the molecule in the absence of additional quenching, and β is the time constant of the bimolecular quenching reaction. The solution has the form

$$N(t) \cong n + n_c = N_0 e^{-\lambda t} \left[\alpha + \frac{\alpha_c \frac{\lambda}{\beta}}{1 + \frac{\lambda}{\beta} - e^{-\lambda t}} \right] \quad (12)$$

$(\alpha + \alpha_c = 1).$

The amplitude of the scintillation is

$$S = \int_0^{\infty} \lambda \eta N dt = \eta N_0 \left[\alpha + \alpha_c F \left(\frac{\beta}{\lambda} \right) \right], \quad (13)$$

where

$$F(x) = x^{-1} \ln(1+x).$$

*It also corresponds to the assumption of any higher order of quenching reaction.

Since $N_0 = E/8$ (see Sec. 4.1) and $S/\eta = E/40$ we have³⁹

$$F\left(\frac{\beta}{\lambda}\right) \approx 1 - \frac{0.8}{\alpha_c},$$

i. e., $\alpha_c > 0.8$ and $\beta/\lambda > 10$. Consequently, the fraction of activations in the "conglomeration" is not less than 80%. If a radius of conglomeration of 20 \AA is assumed, corresponding to the range of an electron with 100 eV energy, the result obtained does not contradict the available calculations.⁸⁸ Next, the scintillation attenuation law (12) yields good agreement with experiment for $\beta/\lambda \sim 10^2$ (Table IX). The high speed of the additional quenching agrees with the previously-mentioned data⁵³ on the temperature quenching of luminescence of polystyrol. To obtain a reliable answer to the question, additional research is necessary.

An analogous analysis can be made also for ionizing particles with high specific energy loss (for example, α particles). In the main track of the particle the individual conglomerations merge and form a common cylindrical column of activated molecules. The fast secondary electrons "split" the track. Retaining the previous scheme,⁸⁴ it is necessary to choose suitable values of the parameters β and α_c . However, the high activation density in the main track may cause certain qualitatively new phenomena. These include quenching by molecules which were "damaged" by the ionizing particle,³⁹ or short-lived products of chemical reactions that occur in the track.^{82, 83} Under the influence of the Coulomb field of the ions and excited molecules, an increase takes place in the probability of intramolecular deactivation.^{52, 82, 83} Additional quenching should also be produced by the local increase in temperature in the track.^{18, 35, 43, 49, 90}

The available experimental data so far do not allow us to establish the relative role of various quenching processes.⁵¹

4.3 Effectiveness of Excitation Energy Transfer in Plastic Scintillators

As ionized particles are slowed down in plastic scintillators, the molecules of the main component are essentially activated. Therefore the amplitude of the scintillation depends substantially on the effectiveness of the transfer of energy of electron excitation from the main component to the additive. To simplify further discussion we shall assume that the additional quenching during excitation by the particles is terminated within a very short time interval (quenching of first order).

Let us consider a plastic scintillator with one additive. The external scintillation amplitude is determined by the relation

$$S_2 = (n_1 T_{12} + n_2) \eta_2 K_2, \quad (14)$$

where n_1 and n_2 are the numbers of molecules of the main component M_1 and of the additive M_2 , excited by the particle in the "fluorescent state"; T_{12} is the effectiveness of the excitation-energy transfer (number of molecules M_2 excited by the transfer, referred to a single excited molecule M_1); η_2 is the quantum yield of M_2 ; K_2 takes into account self absorption in the scintillator. The limiting value of T_{12} depends on the transfer mechanism. In the photon transfer^{1, 91} T_{12} cannot exceed the quantum yield of fluorescence of the M_1 molecules, η_{10} . However, in many papers^{31, 35, 53, 56, 92} it is shown that in a plastic scintillator nonradiative excitation-energy transfer takes place from M_1 to M_2 , the effectiveness of which increases with the concentration of additive and is considerably in excess of η_{10} . If both transfer mechanisms are present simultaneously, T_{12} is determined by the competition between the nonradiative transfer and emission processes on the one hand, and the intramolecular quenching on the other,^{35, 93} i. e.,

$$T_{12} = \frac{K_t + k_e}{K_t + k_e + k_i} = \frac{\eta_{10} + \tau_{10} K_t}{1 + \tau_{10} K_t},$$

where $\tau_{10} = (k_e + k_i)^{-1}$ is the mean lifetime of the excited state of the molecules of the main substance in the absence of the additive, and K_t is the mean probability of nonradiative transfer (per unit time). By definition, the quantum yield of nonradiative transfer is

$$\eta_t = \frac{K_t}{K_t + k_e + k_i};$$

Consequently, the transfer efficiency is

$$T_{12} = \eta_t (1 - \eta_{10}) + \eta_{10} \quad (15)$$

and can reach values close to unity.* (Table X).

According to Krenz's hypothesis³² the high energy transfer efficiency in plastic scintillators is the result of copolymerization of the additive with the main substance (styrol). The energy migrates not between molecules, but within the molecule of the polymer. This point of view is contradictory to many observations which demonstrate that in plastic scintillators, generally speaking, there is no chemical bond between the molecules of the

*It is assumed that the luminescence of the main component is fully absorbed by the additive. In the general case η_{10} should be replaced by η_{10}^P , where $P < 1$.

TABLE X. Quantum yield of nonradiative excitation energy transfer from the polystyrol to the luminescent additive.

Luminescent additive	Exciting radiation	η_t at the following concentration (g/100g of styrol)			Reference
		0,3	1,0	3,0	
Anthracene	UV	0,08			95
3P	UV	0,40	0,50		95
3P	UV	0,24	0,54	0,80	45
3PP	UV	0,28	0,55	0,75	45
	3*)	0,32	0,63	0,85	45
PPO	UV	0,42	0,73	0,84	45

*Normalized for a concentration of 10^{-4} g/g.

additive and of the main substance.^{14, 34, 94} In addition, it is necessary to bear in mind that in a polystyrol or polyvinyl-toluol molecule there are no double bonds in the side chain. There is therefore no π -electron system common to the entire molecule and there is no possibility of energy transfer along the chain through such a system.¹⁷

Formula (15) allows us to calculate the quantum transfer yield η_t from the experimentally-determined transfer effectiveness T_{12} . Belikova and Galanin,⁹⁵ in an investigation of photoluminescence of plastic scintillators with anthracene or n-terphenyl, obtained values of η_t which were in good agreement with theoretical, assuming that the energy transfer was due to "inductive resonance."^{61, 62}

This suggestion is in satisfactory agreement with the experimental results of Swank and Buck,³⁵ Rozman,^{37, 53, 54} Kilin, Prosin, and Rozman,⁶⁶ obtained by excitation with ionizing particles. However, the data available do not permit as yet an estimate of the role of migration of energy in the main substance. Nor are the causes of different concentration dependence of the yield for electrons and α particles still clear.^{35, 37}

In conclusion, a few words concerning the "convenience" of plastic scintillators with spectrum mixers. Owing to the low concentration of the mixer, the energy transferred to it is via the photon mechanism, which leads to a lengthening of the scintillations (Sec. 3.3) and naturally cannot lead to an increase in the luminescence yield. However, because of the reduced self-absorption and change in the spectrum it is possible, generally speaking, to obtain a greater technical efficiency of plastic scintillators with mixers. Let us consider this in somewhat greater detail.⁹⁶ The amplitude of a pulse from a scintillation counter

with a plastic scintillator containing an additive M_2 will, in accordance with (14), be

$$H_2 = (n_1 T_{12} + n_2) \eta_2 K_2 f_2,$$

where f_2 is the mean sensitivity of the photomultiplier to the spectrum of M_2 . For the same plastic scintillator with a spectrum mixer M_3 , we obtain

$$H_3 = (n_1 T_{12} + n_2) \eta_2 \eta_3 K_3 f_3.$$

Consequently, H_3 is greater than H_2 if

$$\eta_3 > \frac{K_2 f_2}{K_3 f_3}.$$

This condition is necessary but not sufficient. It is easy to see that a plastic scintillator with two additives M_2 and M_3 gives a greater pulse than a plastic scintillator with one additive M_3 in high concentration, provided the quantum yield of fluorescence of the substance M_2 is sufficiently large, or, in other words, the photon loss due to intramolecular deactivation in M_2 is less than the loss due to self-absorption in M_3 if the concentration of the latter is large.

5. APPLICATIONS OF PLASTIC SCINTILLATORS

In this section we shall indicate several examples of utilization of plastic scintillators, which should demonstrate the great value of these scintillators both in the practice of scientific experimentation and for technical measurement.

One of the principal problems in the application of scintillation methods for dosimetry of x-rays or γ rays is the question of the tissue equivalence, or the air equivalence of the scintillator.^{97, 98} In other words, is it possible to measure with a scintillation meter the radiation dose in roentgens? Investigations have shown that with "pure" organic scintillators this is possible only for a sufficiently hard radiation (> 250 kev). The combination of a plastic scintillator with a CdWO_4 crystal-phosphor can lower this limit to 80 kev.⁹⁹ A plastic scintillator based on polystyrol with luminescent additives $3P + 4PB$ and with addition of 1/300 of a part of fine grain $\text{ZnS}(\text{Ag})$ has yield variation of not more than - 10% per roentgen of radiation in the hardness interval 20 -- 2000 kev.¹⁰⁰

Plastic scintillators are used to register radiation under high-intensity conditions.¹⁰¹ The absence of "saturation" has been experimentally verified up to a dose intensity of 10^4 /sec.¹⁰² With the aid of thin plastic scintillators one can measure the distribution of depth doses, and also the isodoses of β -active applicators.¹⁰³ Other applications of plastic scintillators for dosimetry of ionizing radiations are reported in references 104 and 105.

Plastic scintillators are used for β -particle counting.^{106,107} For soft β radiation from S^{35} and Ca^{45} it is possible to obtain a counting efficiency two or three times greater than that obtained with gas counters.¹⁰⁸ Plastic scintillators can be used to register electrons in magnetic β spectrometers, and also for β spectrometry.⁴⁷ By way of an example, Fig. 6 shows the pulse spectrum for conversion electrons from Ba^{137} (624 keV), measured with the aid of the PS-2 counter (see Table II) with a FEU-29.⁴⁵

The high hydrogen content of plastic scintillators makes them suitable for counting fast neutrons by the recoil protons.⁴⁸ A telescope of three plastic scintillators was used to measure the energy spectrum of the neutron beam of the synchro-cyclotron target.¹⁰⁹ Plastic scintillators are also used to investigate the spatial and temporal distribution of neutrons in a high-temperature gas discharge.¹¹⁰

By using thin plastic scintillators (to 15 microns) it is possible to count fission fragments against a high background of α particles. The detector has good time resolution.^{111,112} Thin plastic scintillators in conjunction with a thick scintillator serve for particle identification.¹¹³

Plastic scintillators are used in coincidence circuits to study nuclear transformations, in particular, the lifetimes of excited levels.¹¹⁴ The short duration of scintillations more than compensates for the somewhat reduced integrated value of the yield (Fig. 7). A shortcoming is the low cross section of the photoeffect, which in many cases makes it difficult or impossible to separate the γ lines. In this connection, great interest attaches to the attempts of making plastic scintillators with a high content of heavy elements. Unfortunately, they have not yet led to a satisfactory result.^{14,17}

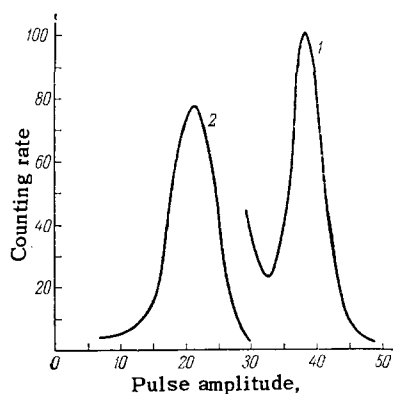


FIG. 6. Pulse spectrum of the PS-2 counter for electrons and α particles.⁴⁵ 1--624 keV electrons, 2--4.90 MeV α particles.

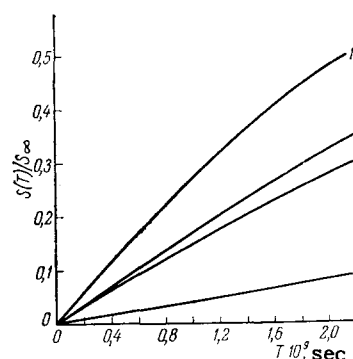


FIG. 7. Fraction of the total number of scintillation photons, emitted within the time interval from 0 to T (ref. 66). Curve 1--PS with 0.015 g/g of 4PB, 2--the same with 3PP, 3--stilbene crystal ($\tau = 6 \times 10^{-9}$ sec), 4--anthracene crystal ($\tau = 25 \times 10^{-9}$ sec)

In conclusion, mention should be made of two other applications of plastic scintillators. To reduce the background of Compton electrons in a scintillation γ spectrometer, the spectrometric crystal together with the γ compound are surrounded by a large plastic scintillator. An anti-coincidence circuit selects only the pulses due to photoelectrons.¹¹⁵ The second case is connected with the possibility of manufacturing thin filaments made of scintillating plastic. Such filaments have properties of light pipes, because of the total internal reflection. A scintillation counter made of a large number of such filaments, can serve to register particle tracks¹¹⁶ in the same manner as a luminescent camera with an electron-optical converter.¹¹⁷

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