

## The plastic scintillator activated with fluorinated 3-hydroxyflavone

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*Received November 30, 2016*

A new radiation-hard plastic scintillator (PS), based on polystyrene and activated with fluorinated 3-hydroxyflavone, is presented. The new scintillator has the light output half-attenuation dose equal to 11 Mrad, which is much more than a similar PS, containing 3-hydroxyflavone. Also, the temporal characteristics of the PS are investigated. The scintillation flash rise time was 0.5 ns, what is much faster than the rise time of conventional PS, equal to about 0.9 ns. Such properties of the new PS are achieved by application of fluorinated 3-hydroxyflavone as an activator.

**Keywords:** plastic scintillator, radiation hardness, rise time.

Представлен новый радиационно-стойкий пластмассовый сцинтиллятор (ПС) на основе полистирола, активированный фторированным 3-гидроксифлавоном. Сцинтиллятор имеет дозу половинного ослабления светового выхода 11 Мрад, что значительно больше, чем у аналогичных ПС с содержанием 3-гидроксифлавона. Исследованы временные характеристики данного ПС. Фронт нарастания сцинтилляционной вспышки составил 0,5 нс, что значительно быстрее фронта нарастания для обычных ПС, равно примерно 0,9 нс. Такие свойства ПС достигнуты использованием в качестве активатора фторированного 3-гидроксифлавона.

**Пластмассовий сцинтилятор з фторованим 3-гідроксифлавоном.** Ю.А.Гуркаленко, Д.А.Єлісеєв, П.М.Жмурін, В.М.Переїмак, О.В.Свідло.

Представлено новий радіаційно-стійкий пластмассовий сцинтилятор (ПС) на основі полістиролу, активований фторованим 3-гідроксифлавоном. Сцинтилятор має дозу половинного ослаблення світлового виходу 11 Мрад, що значно перевищує дозу у аналогічних ПС із вмістом 3-гідроксифлавоном. Досліджено часові характеристики даного ПС. Фронт наростання сцинтиляційного спалаху складає 0,5 нс, що значно швидше фронту наростання для звичайних ПС (приблизно 0,9 нс). Такі властивості ПС досягнуто використанням в якості активатора фторованого 3-гідроксифлавоном.

### 1. Introduction

Plastic scintillators (PS) are widely used for manufacturing of detecting devices in high-energy physics experiments [1]. Particle physics development goes on both by studied particles energy increase, and by accelerated particles beam luminosity increase. At the present time energy of 15.4 TeV ( $15.4 \cdot 10^{12}$  eV) releases as a result of collision of two protons on colliding

beams of the Large Hadron Collider LHC (CERN, Switzerland) at the integral luminosity of  $1.7 \cdot 10^{34}$  cm<sup>-2</sup>s<sup>-1</sup> [2]. At such total radiation effect on the closest to the beam axis PS can reach of 10 Mrad for 10 years of detector operation [3]. After planned upgrade in 2016–2018 years the LHC beam protons energy will double, and the luminosity will increase on the order [4]. Accordingly, the total dose of irradiation on

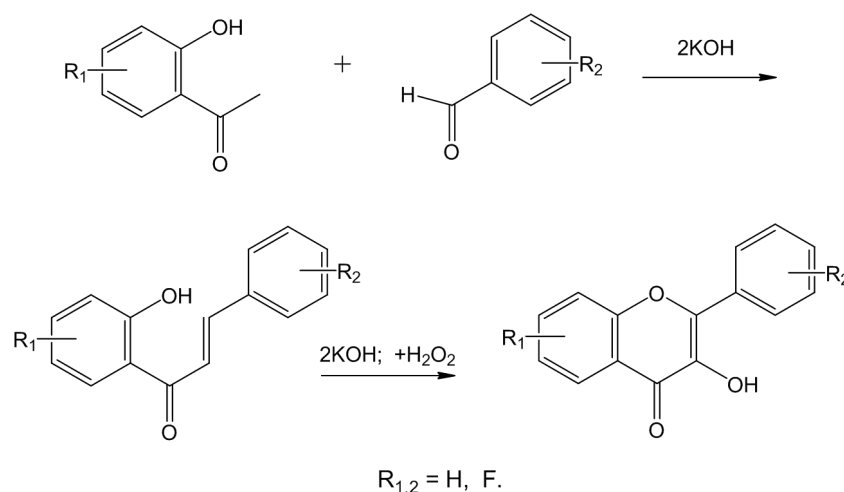


Fig. 1. The scheme of the Algar-Flynn-Oyamada reaction.

mounted particle detectors will increase on the order. Therefore, the question of improving the radiation hardness of the scintillation material turns to be very actual.

For conventional plastic scintillator (PS), the radiation hardness (after J.B.Birks' definition, this is absorbed dose value, at which the light yield of scintillator decreases in two times) does not exceed few Mrads [5]. This is because, under influence of irradiation in polystyrene-based PS, defects are formed, which are able to absorb over a wide spectral range. Moreover, this spectral range coincides with the absorption and emission ranges of the PS polystyrene base activator, and partially with the radiation area of the PS shifter. Therefore, under irradiation, the formed defects both reduce the transparency of polystyrene on the PS basic wavelength (420 nm), and compete with the activator in interception of excitation energy formed by interaction of high-energy particles with the PS polymeric base [6]. Therefore, one of ways to increase the radiation hardness is associated with search for more stable activator substances, able to effectively absorb the excitation energy of polystyrene, and radiate in the spectral ranges, free of absorption bands of the induced defects. 3-hydroxyflavone is one of these substances. Early experiments have shown that use of such substances as the activator of the PS polystyrene basis can increase the radiation hardness threshold in almost three times. In addition, the performed experiments showed that the presence of fluorine in the composition of 3-hydroxyflavone molecules positive effects on the radiation hardness parameters of plastic scintillators, containing them [7]. Therefore,

the main objective of the work was to test the effect of the presence of fluorine in the 3-hydroxyflavone molecule structure on the radiation hardness properties of scintillator compositions, containing it.

## 2. Experimental

*Sample preparation.* Fluorinated flavones synthesis methods were used, which allow to introduce the fluorine atom into the phenyl and chromenone part of the 3-hydroxyflavone molecule (3HF).

Thus, for the synthesis of fluorinated hydroxyflavones, a conventional method was used, with using 2-hydroxyacetophenones and benzaldehydes, described for example in the work [8]. Formed in this way *o*-hydroxyphenylstyrylketones were oxidized with hydrogen peroxide into flavones through dihydroflavones by the known Algar-Flynn-Oyamada reaction, showed in Fig. 1 [9–11].

Based on this scheme, to introduce the fluorine atom in the phenyl part of the 3HF molecule, commercially available benzaldehydes containing fluorine atoms at various positions were used. For introducing the fluorine atom into the benzene ring of the chromenone part, 5-fluoro-2-hydroxyacetophenone was synthesized by acylation of 4-fluorophenol, followed by the Fries rearrangement, shown in Fig. 2, in the presence of anhydrous aluminum chloride [12, 13].

The starting material 4-fluorophenol was obtained in the good yield from commercially available anilines by its diazotization with substitution of the amino group by the fluorine atom by the known Schiemann method. The obtained fluorobenzene under-

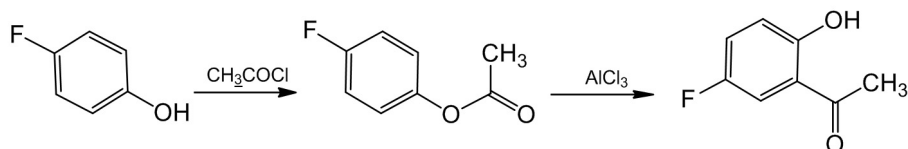


Fig. 2. The scheme of the Fries rearrangement.

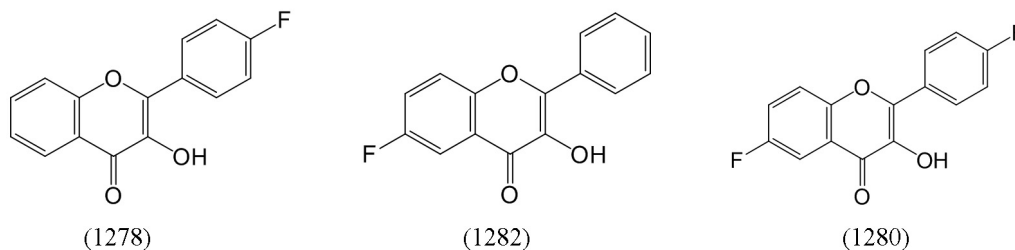


Fig. 3. The synthesized 3HF derivatives, used as PS activators.

good bromination followed by hydrolysis of 1,4-fluorobromobenzene in an autoclave with alkali agents and a copper catalyst under conditions described in [14, 15]. So, we have synthesized three modified trihydroxyflavone substances, the structural formula of which is shown in Fig. 3.

The synthesized substances were used as the activator of polystyrene plastic scintillators. Samples were prepared by radical bulk polymerization of styrene and 2 wt.% of activator substances. To do this, in a glass vial fresh-distilled styrene was placed. Then 2.0 wt.% of corresponding 3-hydroxyflavone and 2.0 wt.% *p*-terphenyl were added. The content of the vial was dissolved at  $T = 75^\circ\text{C}$ , then purged with argon for 6 min. After this, the vial was sealed and placed into an air polymerizer, heated to  $130^\circ\text{C}$ . After 2 h, the temperature was increased to  $155^\circ\text{C}$  and kept for 3 days. The process was observed visually. After holding, the temperature was reduced to  $90^\circ\text{C}$  at the rate of  $5^\circ\text{C/h}$ , held for 2 h, and then heating was excluded. After cooling to room temperature, the vial was broken and the sample was separated of glass. From the obtained samples, the PS samples with the shapes of cylinders with diameter of 16 mm and a height of 10 mm and polished on all sides to optical purity.

*The optical properties of the scintillation samples.* The excitation spectra and luminescence spectra of the samples activated with the 3-hydroxyflavone derivatives were obtained using a spectrofluorimeter Fluoro-Max4 (Fig. 4).

Fig. 4 shows that introduction of fluorine into the 3-hydroxyflavone molecular structure hardly changes its luminescence

spectrum in the polystyrene medium. At excitation in the range of 360 nm, a broad luminescence band with the peak wavelength of 530 nm is observed. This character of the luminescences characteristic for 3HF molecules. However, the excitation spectrum of fluorinated 3HF molecules luminescence is substantially modified. Thus, fluorine introduced into the phenyl part of the molecule 3HF (1278) gives rise to a flection in the excitation band at a wavelength of 390 nm, which starts to form an observed single peak in the presence of fluorine in the 3HF molecule hromene fragment (1282) (Fig. 2). The observed peak in the excitation band shifts to longer wavelength range of near to 400 nm, with the presence of fluorine in the hromenone and phenyl part of the 3HF molecule (1280). Thus, fluorine introduction into 3HF molecule structure significantly expands the range of the luminescence excitation to 400 nm, what makes it possible to use these molecules to create wavelength-shifting transport media of different kinds.

*The scintillation properties.* The temporal characteristics of the scintillation samples were measured by time-correlated count. As the start pulse, Cherenkov signal, produced by fast electron, was used, and as the stop — scintillation response of the sample (Fig. 5).

The plastic scintillator timing measurement results are shown in Fig. 6.

In Fig. 6 it is seen that the introduction of fluorine in the molecule structure 3HF not significantly affect the temporal characteristics of the observed luminescence. The average value of the scintillation pulse decay time is 7 ns. But the rise time of the scintillation pulse significantly has short-

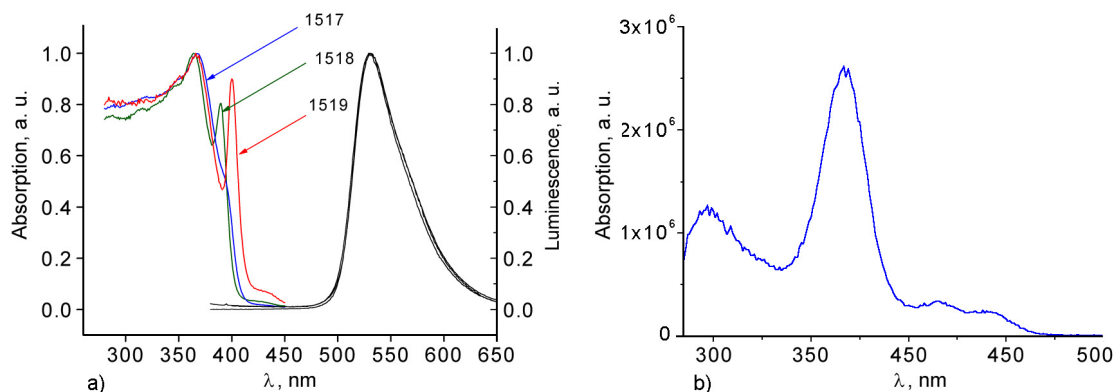


Fig. 4. a) The absorption and luminescence spectra of polystyrene based plastic scintillators, activated with 2 wt.% 3HF derivatives 1278 (the sample number 1517), 1282 (the sample number 1518), and 1280 (the sample number 1519), b) the absorption spectrum of the 3HF molecule.

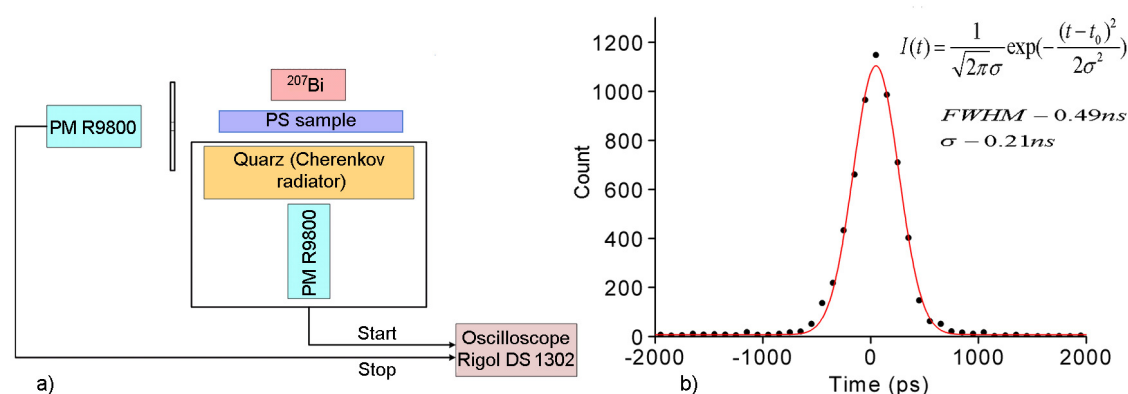


Fig. 5. a) The scheme of PS the temporal characteristics measurements setup and b) its instrumental response function.

ened and is about 0.5 ns, compared with a rise time of 0.9 ns for a conventional plastic scintillator. If to restore the function of the scintillation pulse excitation, which has the shape of the Gaussian distribution, by fitting the experimental points by convolution with the decay function [16], then even shorter rise time will be obtained (Fig. 7).

Traditionally, the scintillation pulse rise time is determined by timing parameters of the process of recombination of charges generated in interaction of high-energy charged particles, formation of the excited states, and the time of nonradiative transfer of excitation energy to the plastic scintillator activator. But there is another way of excitation of the activator in a polystyrene-based plastic scintillator [17]. And this way is associated with direct electron capture by the activator molecule with following diffusion of the "hole", with recombination of the charge on the molecule activator with transfer it into the excited state. And as the authors noted, this channel of excitation production is much faster than the traditional

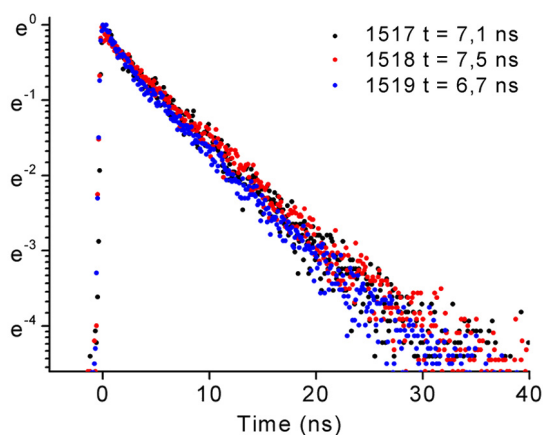


Fig. 6. The scintillation flash decay curves of the polystyrene PS, activated with fluorine-modified 3HF.

channel. As the activator to conventional plastic scintillator paraterphenyl is used, molecules of which have weakly expressed electron affinity as compared to the molecules of 3-hydroxyflavone derivatives.

Table. The light yield and the radiation hardness of the plastic scintillators, measured immediately after irradiation

Compound	0 Mrad	5.0 Mrad	L5/L0, %	$D_{1/2}$ , Mrad
2 % (1278)1F	80	49	61	7.0
2 % (1280)2F	55	48	87	11.4
2 % (1282)1F	59.5	41	69	9.3
2 % 3HF				7.3

Therefore, the observed shortening of the rising edge of scintillation flashes can be attributed to the immediate annihilation of charge on 3-hydroxyflavone molecules.

*The radiation hardness.* To establish the radiation hardness threshold of the plastic scintillators with the 3HF derivatives, they were subjected to gamma irradiation of a cobalt gun at the radiation dose rate at the level of 1.2 krad/h. The total absorbed dose in irradiated samples was 5 Mrad. The results of measurements of light output changes before and after irradiation are presented in Table.

The measurement results show (Table), that introduction of the fluorine only the into phenyl part of the 3HF molecule does not change the radiation hardness threshold, while introduction of the fluorine in hromenone fragment of the 3HF molecule increases the threshold of radiation hardness from 7.3 Mrad for PS activated 2 wt. % 3HF to 9.3 Mrad. And the substance, used as the activator of a plastic scintillator and having the fluorine in the hromenone and phenyl fragment of the 3HF molecule, increases the threshold of the radiation hardness up to 11 Mrad. This is the significant value when you consider that the radiation hardness of conventional plastic scintillators is less than 3 Mrad.

### 3. Conclusions

The measurements showed that use as the activator of the plastic scintillator fluorine-modified 3HF derivatives, can lead to improvement in the properties of the plastic scintillator in terms of both improvement of the radiation hardness characteristics and improvement of its timing. These plastic scintillators with 3HF derivatives, containing the fluorine in the hromenone and phenyl molecule fragments, raise the threshold of the radiation hardness up to 11 Mrad, compared with 7 Mrad for the similar plastic scintillator, activated with unmodified 3HF.

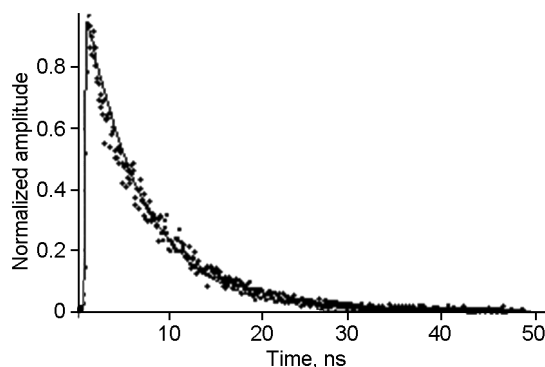


Fig. 7. The approximation of experimental dots of the scintillation pulse decay curve by expression

$$I(t) = A \int_0^t \exp\left(-\frac{(t-t')^2}{2\sigma^2}\right) \exp\left(-\frac{t-t'}{\tau}\right) dt',$$

where  $A$  is the pulse amplitude,  $t_0$  — the center of Gauss distribution,  $\sigma$  — the standard deviation, and  $\tau$  is the luminescence decay time of 3HF molecules.

Also, fluorinated 3HF molecules have much higher affinity to electrons relatively to molecules of conventional activators, what shortens the scintillation rise time to 0.5 ns from 0.9 ns of conventional plastic scintillators.

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